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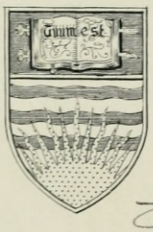

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Molecular Spectra and Molecular Structure

A GENERAL DISCUSSION

HELD BY

The Faraday Society

September, 1929

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MOLECULAR SPECTRA AND MOLECULAR STRUCTURE

A GENERAL DISCUSSION

ERRATA.

Page 645, line 2. For *An* Σ read *An E*.

Page 771. At bottom after "uniform system" add: To distinguish between emission and absorption bands, if for example one uses $^2\Pi \rightarrow {}^2\Sigma$ for a certain emission transition, one might use $^2\Pi \leftarrow {}^2\Sigma$ for the same transition in absorption, putting in each case the upper level (here $^2\Pi$) first.

Page 798. In both tables $\Delta\nu$ should be inserted in the heading to the last two columns.

Page 835. Insert the following footnote:—

(*Note added 16th December*, 1929.)

A paper recently published by Pringsheim & Yost (*Z. Physik*, 58, 1, October, 1929) gives values for the Raman Lines from aqueous solutions of SO_4 ions. For solutions of sulphates their results agree well with the above, but for sulphuric acid the agreement is not so good. This is probably due to the fact that their measurements were made with sulphuric acid of strength 12 Mols. per litre, whereas mine were on the one hand with pure sulphuric acid and on the other, with dilute sulphuric of strength approximately 5 Mols. per litre.

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A GENERAL DISCUSSION.

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MOLECULAR SPECTRA AND MOLECULAR STRUCTURE.

A GENERAL DISCUSSION.

A GENERAL DISCUSSION on "MOLECULAR SPECTRA AND MOLECULAR STRUCTURE" was held by The Faraday Society on 24th and 25th September, 1929, in the Physics Department of the University of Bristol. PROFESSOR T. M. LOWRY, F.R.S., PRESIDENT, was in the Chair.

GENERAL INTRODUCTION.

BY PROF. W. E. GARNER AND PROF. J. E. LENNARD-JONES.

Received 10th September, 1929.

1. General Characteristics of Molecular Spectra.

Perhaps one of the most successful applications of the new wave mechanics has been the unravelling of many of the complexities of molecular spectra. In consequence it has given a great impetus to experimental work in this field, and has led to results of great importance to the physicist and the chemist. Nevertheless the interpretation of molecular spectra has necessitated a considerable array of symbols, which certainly appear forbidding to those whose researches have not lain in this field. This introduction is intended for those who have not specialised in the subject, but who yet wish to understand sufficient of the experimental and theoretical methods to be able to appreciate the results obtained.

The spectra of molecules exhibit certain general characteristics which are analogous to the spectra of atoms. When, as in atoms, the spectra are analysed into terms, there appear a number of molecular levels, analogous to the levels in atoms, due to different electronic configurations and must almost certainly be due to a series of different electronic configurations. The difference between these *electronic* levels may be anything from about one to ten volts or more. As in atomic spectra the various electronic levels may be multiplets, the order of the interval between the various members being small in the lighter atoms, but as large as a volt in heavy molecules and possibly of the same order as the interval between different electronic levels.

With each electronic level of a molecule is associated a group of neighbouring levels, fairly regularly spaced at intervals of about one-tenth of a volt (though this figure is given merely as a rough indication

of the order of magnitude involved in a typical case; actually, there may be considerable fluctuations about this figure). These levels are interpreted as being due to the sequence of possible quantised *vibrations* of the molecules with the same electronic configuration, and the formula for the energy of a simple oscillator according to quantum mechanics, $E_v = h\nu(n + \frac{1}{2})$, is found to be approximately applicable, at any rate for small values of n. The frequency of vibration of the molecule can thus be easily deduced from a measurement of the energy intervals in the group.

Again, each vibration level itself consists of a group of levels, due to the sequence of possible quantised *rotations* of the molecule with the same electronic configuration and the same energy of vibration. The energy interval between these levels is usually of a much less order of magnitude than those already considered (say, one-thousandth of a volt), though in light molecules like He_2, it may be large. To a first approximation, the rotation energy levels are those of a quantised rotator, *viz.*, $E_r = h^2K(K + 1)/8\pi^2I$, where I is the moment of inertia and K the rotation quantum number. The measurement of the energy intervals in a rotation band thus leads to a determination of the moment of inertia of a molecule.

Finally, each rotational level shows a fine structure, and the higher the rotational level the greater the splitting which occurs. The character of this splitting is of great assistance in determining the nature of the corresponding electron term, just as the behaviour of an *atomic* level in a magnetic field determines its character.

Transitions from a rotational level of one group to the rotational levels of another group give rise to a single band. Not all of such conceivable transitions are represented in the molecular spectra. There are, as in atoms, certain selection rules which govern the transitions which actually occur. In some homopolar molecules (for example, He_2) alternate rotation levels are missing, while in others (H_2), the rotation levels are alternately strong and weak. The study of alternating intensities and alternating missing lines in band spectra has proved a very valuable source of information about nuclear spins, and the results obtained to date are discussed by Mulliken (page 634).

In view of the different orders of magnitude of the energy intervals between electronic, vibration and rotation levels, the technique required in the investigations of transitions between electronic levels is different from that for transitions between vibration and rotational levels. Electronic bands usually lie in the visible or ultra-violet region, whereas changes of energy of vibration and rotation give rise to bands in the infra-red. A study of absorption bands in the infra-red gives information about the vibration and rotation levels in the lowest (unexcited) electronic state. It is thus of great value, for it is more difficult to deduce information about the ground state from electronic transitions; in many cases such electronic bands lie in the ultra-violet where high dispersion is not available.

The discovery of the Raman effect has placed a new weapon in the hands of the experimentalist, for he can now study transitions between oscillation levels by means of light in the visible spectrum, where the technique is highly developed. Observations of the intensities of the Raman lines in some cases confirm the results obtained from band spectra as to the relative weights of the various rotational levels, but in the case of nitrogen, investigated by Rasetti, there is a serious discrep-

ancy as yet unexplained. Rasetti [1] has recently reported a pure electron transition due to Raman scattering, *viz.*, a transition between the doublet levels of NO in its normal (^2P) state.

The three broad groups into which the discussion is divided correspond to the three types of experimental method adopted to investigate the various regions. It is hoped that the discussion will bring out the degree of confirmation or discrepancy between the results so far obtained and will indicate problems of theoretical importance, which require further more detailed investigation.

2. Notation and Band Spectra.

(*a*) *Atomic Spectra.*

Unfortunately, a general notation for band spectra has not yet been adopted and, as it is impossible to review all the notations which are in use, this report must only deal with the general principles which have been followed. The obvious course is to follow as closely as possible the methods and notations which have been so successful in the unravelling of atomic spectra, but part of the difficulty in doing so has been to find appropriate quantum numbers for electrons in a complicated system like a molecule. In an atom this was relatively easy, as it was possible to work out exactly the theory of the hydrogen atom and the quantum numbers required to specify the sequence of possible states could be applied to the electrons in more complicated atoms. Thus in the Bohr theory, the possible orbits of the hydrogen atom could be described in terms of a principal quantum number n, an azimuthal quantum number k, and a magnetic quantum number m. Fortunately the Schrödinger theory introduces the same quantum numbers, though it is not so easy to ascribe a meaning to them. (One important modification may, however, be noticed, *viz.*, that $l = k - 1$ appears where formerly k appeared and this has removed many difficulties connected with selection rules.) Later it was found necessary to supplement these quantum numbers by a fourth, which is now generally regarded as being due to the spin of the electron. The fourth quantum number can, therefore, be taken to be the vector s describing this spin (in terms of $h/2\pi$), or alternatively, the vector j describing the resultant angular momentum, that is, the "orbital" angular momentum plus spin. The great principle which seems to govern the theory of atom-building is Pauli's Exclusion Principle, according to which no two electrons in an atom can have the same four quantum numbers. As the spin quantum number only allows of two possibilities according as the direction of spin is plus or negative, this implies that there are in an atom not more than two electrons with the same n, l and m. n takes the values 1, 2, 3 . . ., as the various atomic shells are built up.

In the later theories [2] these quantum numbers have been modified, but the main results obtained by the scheme outlined above are not affected except as regards fine structure, and, in particular, the model of the spinning electron is found to have a firm theoretical foundation.

When there is only one electron in an atom, or when there is only one electron outside a closed shell, the spectral terms or levels are denoted by S, P, D . . ., according as $l = 0$, 1, 2 . . ., and all the

[1] *Nature*, **124**, 93, 1929.
[2] Dirac, *Proc. Roy. Soc.*, A. **117**, 610, 1928; **118**, 351, 1928.

levels, except the S-levels, are doublets owing to the two directions of spin possible for the electron, along and opposed to the angular momentum or "orbital" vector. As $l = 0$ for the S-levels, the two members of the S doublet are coincident.

Instead of describing the individual electrons in terms of the quantum numbers, it is found best in practice to classify electrons into the types, s, p, d . . ., electrons according as $l = 0, 1, 2 \ldots$, corresponding to the S, P, D . . ., notation for spectral terms. The principal quantum number, when known, is written in front of this symbol, as in $1s$, $2p$, $3p$, $3d$. . . .

When there are several electrons of the same n but different l values outside a closed group, that is, several electrons in an uncompleted shell, the method of determining the spectral type, which has proved most successful, is to assume (1) a strong coupling between the "l" value of the individual electrons. This gives rise to a number of possible vector sums of the "l" values, the resultant being denoted by L, and L determines the spectral type. The terms are S, P, D . . ., according as $L = 0, 1, 2 \ldots$ Next, it is assumed that there is (2) an independent coupling between the spins of the electrons and finally (3) a perturbation between the resultant *angular momentum* vector and the resultant *spin* vector. This process determines the multiplicity of the term. For, the coupling between the spins produces a resultant spin vector S and this may have $2S + 1$ quantised components along L. The resultant of S and L, denoted by J, may therefore also have $2S + 1$ different values and therefore the multiplicity of the term is $2S + 1$.

In the nitrogen atom, for example, there are two electrons in the level of principal quantum number 1 (closed group), two in the level $n = 2$, $l = 0$, $m = 0$ (closed group), and three outer electrons distributed between the three other levels, which have $n = 2$, *viz.*, those for which $l = 1$ and $m = 1, 0$ and -1. The three possible values of L are then 0, 1 and 2 and the corresponding spectral terms are S, P and D. The spin vector S may be $3/2$ or $1/2$, as each of the three outer electrons has a spin of one-half a unit and all may point in one direction or two may point in one direction and the third in the opposite direction. The possible multiplicities are, therefore, 4 and 2, so that combining this with the previous result, we expect the following spectral terms for the nitrogen atom, ^4S, ^2S, ^4P, ^2P, ^4D and ^2D.

This method has, however, so far neglected the Pauli Exclusion Principle, and this precludes some of these terms, as, for instance, ^4P which would require two electrons to have the same four quantum numbers. This consideration reduces the possible terms to ^4S, ^2D and ^2P.

When these vector methods are applied to a quantitative calculation, the indication is that the ^4S term is the lowest, then ^2D and finally ^2P. In general, we may say that that term is the lowest which has the highest multiplicity and of those terms which have the same multiplicity, that term is lowest which has the greatest L value. (In N, $^2D < {}^2P$, because in the D term $L = 2$, and in the P term $L = 1$.)

These vector methods have now been replaced by Heisenberg's *resonance theory*. The general idea of this theory (which is a logical consequence of the new quantum mechanics and had no place in the older theory) is that the state of an atom in which an electron 1 is in one prescribed level and an electron 2 in another prescribed level is indistinguishable from that state of the atom when electron 1 is in the second level and electron 2 is in the first level. These two atomic states have

the same energy and are said to be *degenerate*. Now, whenever two states of an atom are degenerate and a perturbation is introduced (say by an applied electric field) the degeneracy is removed and the new mechanics gives the difference between the two levels which appear in place of the one existing before. In the case referred to, the Coulomb field between the electrons themselves produces the perturbing field and removes the degeneracy. It is found that the lower level always corresponds to the greatest spin vector S and so to the greatest multiplicity. Without entering into a more detailed discussion of the resonance theory, we may say that it confirms the results obtained qualitatively by the vector methods above described and in addition gives the right quantitative results, as, for example, in the para- and ortho- states of helium.

(*b*) *Molecular Spectra.*

In a diatomic molecule, it is the component of the angular momentum l along the nuclear axis (previously denoted by i_{l_τ}, σ_{l_τ}, etc., but now denoted by λ), which determines the spectral type. When for one electron, this component vanishes, the spectral term is denoted by Σ (to parallel the S of atoms, although some authors also use S in this connection). For $\lambda = 1, 2, \ldots$ the terms are Π, Δ. . . . When several electrons are present, it is the sum of the components ($\Sigma\lambda$) which determines the spectral type, being Σ, Π, Δ . . . according as $\Sigma\lambda$ (now denoted by Λ) $= 0, 1, 2. \ldots$ When the components of the individual electrons are known, the electrons are said to be σ, π, δ . . . electrons according as $\lambda = 0, 1, 2. \ldots$ The multiplicity is determined, as in atoms, by the resultant spin vector S. In many cases S may be regarded as strongly coupled to the nuclear axis, owing to the strong coupling between S and the Λ vector. This case, referred to as *nuclear axis coupling*, always occurs when there is no rotation of the molecule as a whole and when $\Sigma\Lambda > 0$. The number of different quantised components of S along the axis is equal to the multiplicity. The multiplicity is denoted as in atoms; thus, $^2\Pi$, $^3\Delta$, and so on. When it is necessary to distinguish the different members of a multiplet, this is done by means of a suffix which is equal to the possible resultant components of S and Λ along the axis, as in $^2\Pi_{3/2}$, $^2\Pi_{1/2}$. Sometimes the coupling of S along the axis is weak and then S may be coupled with the resultant angular momentum vector (denoted sometimes by p_l, sometimes by j_k, but preferably by K as in Mulliken's paper (page 634), and equal to the angular momentum of the molecule as a whole, *regarded as a top*). This case is referred to as *rotation axis coupling*. Examples of both types of coupling occur in the helium molecule.

In the case of He_2, it appears that in the higher rotational levels the "l" values are uncoupled from the nuclear axis ("l-uncoupling"), but it has not been observed in the case of other molecules. The L value of the atoms must then be combined with the nuclear rotation, and S may be coupled to the resultant.

The vibrational quantum number is usually denoted by n, although the same symbol is also used for the principal quantum number, but the interpretation is usually obvious. The symbol in general use for the rotational quantum number is j, though as Mulliken suggests in his paper, it would perhaps be better to use a new symbol K, as j is likely to be confused with the J used in atoms for the quantum number of

the total resultant angular momentum. Every energy level in a molecule can then be specified by (i) the electronic configuration or the spectral term, (ii) the vibrational quantum number n, (iii) the rotational quantum number K. The electronic configuration is, however, usually difficult to find and, in general, it is only possible to specify the type of spectral term, $^1\Sigma$, or $^2\Pi$, etc., with an indication of its energy relative to other known levels. Some progress has been made with the problem of electronic configuration; this must now be referred to.

(*c*) *Electron Configuration in Molecules.*

We have already said that when the component of the angular momentum of an electron about the nuclear axis is 0, 1, 2 . . ., it is described as a σ, π, δ . . . electron. In order to specify an electron more precisely Hund and Mulliken consider the configuration which arises when the two atoms of a molecule are pushed together to form one united atom. The ordinary atomic quantum numbers can then be used to describe the electronic levels, or alternatively the notation ns, np, nd. . . . Furthermore for this case the sequence of energy levels, $1s$, $2s$, $2p$, $3s$, $3p$, $3d$ . . ., is known, and it is possible to deduce the energy levels into which these atomic levels split up as the nuclei are pulled slightly apart. Each s level becomes a σ level, a p level becomes a π level or a σ level and so on. The possible levels must therefore be denoted by 3 symbols as in $2p\pi$, $3d\sigma$. . . . Hund writes the levels in the order $1s\sigma$, $2s\sigma$, $2p\sigma$, $2p\pi$, $3s\sigma$. . . . Each σ-level can contain two and only two electrons (of opposite spin) if the Pauli Principle is to be preserved, but a π-level or a δ-level, etc., can contain four on account of the two possible directions of the angular momentum vector and the two possible directions of electronic spin. An electronic configuration can then be written in the form, $1s\sigma^2$, $2s\sigma^2$, $2p\sigma^2$, $2p\pi^4$ . . . where the index gives the number of electrons in a given level. Whenever a configuration consists of closed groups, as in the example given, the resulting spectral term is a singlet Σ term ($^1\Sigma$), as the resultant angular momentum is zero, and the resultant spin vector is zero. Examples of such configurations are H_2, He_2, and N_2 in the ground states.

The sequence of energy levels changes as the internuclear distance is increased, but by considering the other limiting case, which is known, *viz.*, that of infinitely distant atoms, and making suitable interpolations for the intermediate distances actually realised in molecules, Hund (and Mulliken independently) has deduced a series of energy levels for a number of diatomic molecules.

3. Selection Rules.

In order to interpret the bands of a molecular spectrum, it is essential to know what transitions are theoretically possible. It is one of the great advantages of the wave mechanics that it indicates in most cases, unambiguously, which transitions are to be expected and which are not, whereas the older quantum theory had to be supplemented by a number of *ad hoc* selection rules. In the case of atomic spectra, the selection rules may be summarised as follows: (1) all changes in principal quantum n are possible; (2) when only one electron changes its level, l must change by ± 1 ($\Delta l = \pm 1$), and when several electrons change their levels simultaneously, the sum of the changes of all of the individual l values must be an odd number (Russell-Laporte rule);

(3) intercombinations only take place between terms of like multiplicity (singlets to singlets, triplets to triplets, etc.) (although exceptions may occur when the energy differences between the members of a multiplet are large); (4) intercombinations between the various levels of a multiplet are governed by the rule $\Delta j = 0$ or ± 1, where j is the inner quantum number (or the total angular momentum of the atom).

Most of these rules were found empirically before the advent of the wave mechanics, but they have been shown to possess a theoretical foundation; in particular, Wigner and others have given a simple explanation of the rule governing changes in l. As this interpretation has led to a theoretical generalisation applicable for molecules as well as atoms, it is necessary to mention briefly the fundamental ideas.

In a one-electron problem, the possible energy levels are obtained from a consideration of a certain differential equation in three space co-ordinates, which determine the position of the electron. To each energy level corresponds an *eigenfunction*, which is a function of the particular co-ordinates chosen. This *eigenfunction* associates a definite numerical value, positive or negative, with every point of space. It is found that these *eigenfunctions* fall into two classes. In one class, the *eigenfunction* has the same value and the same sign for every pair of points which are images in the origin of co-ordinates. These *eigenfunctions* are said to be positive (Wigner) and the term level is said to be positive. In the other class, the *eigenfunction* has the same absolute value but the opposite sign for each pair of image points. These are said to be negative. Furthermore, the *eigenfunctions* are positive when the quantum number l is even and negative when it is odd.

The *eigenfunction* of a number of electrons is equal, to a first approximation, to the product of the *eigenfunctions* of the individual electrons. The *eigenfunction* of the electrons in an atom is therefore positive or negative according as Σl is even or odd. This result must still be true when the interaction of the electrons is taken into account, for that cannot modify the symmetry properties of the total *eigenfunction*.

Simple considerations based on wave mechanics show that *only those transitions are possible, in which a positive term changes to a negative term.* This simple result contains the Russell-Laporte Rule given above, for it implies that the sum of the l values must change from an even number to an odd number, or *vice versa*.

In a recent paper, Wigner and Witmer have extended these ideas to molecular spectra, though the problem is necessarily more complicated than that of atomic spectra, owing to the fact that the molecule can rotate as a whole. This rotation in wave mechanics is itself represented by an *eigenfunction*, and has a characteristic quantum number, sometimes denoted by j and sometimes by K. For one set of values of K, the *eigenfunctions* are unaltered when the nuclei are interchanged, and for the other set, the *eigenfunctions* change their sign on interchanging the nuclei. The former set is said to be symmetrical in the nuclei, and the latter anti-symmetrical. *Theory shows that when the nuclei are identical*, that is, in homopolar molecules, *intercombinations between the two sets do not take place;* in other words, terms which are symmetrical in the nuclei combine only with other symmetrical terms, and antisymmetrical only with antisymmetrical. At the same time, it is found that just as in atoms, positive terms combine only with negative and negative with positive.

From these general rules, it follows that when the electronic levels are both Σ levels (that is, have zero moment about the nuclear axis), the rotational quantum number K can change only by ± 1. The band for which K increases by 1 on emission is called a P branch, the other an R branch. Further, in the case of equal nuclei, transitions between Σ levels are only possible when one has a positive symmetry and the other negative symmetry. An important example is to be found in the spectrum of H_2. The Lyman bands arise from transitions between the two lowest known levels of hydrogen and have only P and R branches. As the lowest state of H_2 is known to have positive symmetry and to be a Σ state, it follows that the upper lower level must also be a Σ state and must have negative symmetry. When there is a change of angular momentum about the nuclear axis as in a transition $\Pi - \Sigma$, K may change by 0 or by ± 1. These correspond to the three observed sets of bands called P, Q, and R branches. All three branches may occur without change of angular momentum about the axis (except in Σ case), provided there is a change of symmetry in the term, as in $\Pi_+ - \Pi_-$.

As in atomic spectra, intercombinations only take place between terms of like multiplicity. For example, the hydrogen molecule spectrum has two non-combining sets, a singlet and a triplet set, in close analogy to the spectrum of helium. For transitions between the components of a multiplet, the selection rule is $\Delta j = 0, \pm 1$ as always.

4. Band Spectra and Atomic Nuclei.

We have already said that the *eigenfunctions* for a rotator consist of two non-combining sets, a symmetrical and an antisymmetrical set. This is strictly true only when nuclei are assumed identical and not to have a spin. It applies, for instance, to the helium molecule, whose nuclei, consisting of four protons and two electrons, possess no resultant spin. Theory is in complete accord with observation in this case, for it has long been known that the band spectrum of helium possesses only half the lines which would normally be expected, alternate lines being absent. Moreover, it is the symmetrical levels which are absent. In other homopolar molecules, however, both sets of rotational levels occur, the weight of one set being appreciably larger than the other. In hydrogen, one set has three times the weight of the other.

These facts have been completely accounted for by Heisenberg on the assumption that each nucleus has a spin in the case of H_2 of half a unit $(h/4\pi)$. Each nucleus must therefore be given an *eigenfunction* in spin, and the *eigenfunction* of a two nuclear system is the product of both. When all possible combinations of two such *eigenfunctions* are considered, it is found that three are symmetrical and one antisymmetrical in spin; that is, in three cases the *eigenfunction* is unchanged when the nuclei are interchanged and in the other case, the sign is changed. The symmetrical set must be regarded as having three times the weight of the antisymmetrical set.

If now the *eigenfunctions* of nuclear spin are combined with the *eigenfunctions* of rotation as a whole, and it is assumed that the total *eigenfunction* must be antisymmetrical in the nuclei, the facts of the alternating intensities in the spectrum can be completely accounted for.

This rule is only part of a more general rule, which has been found to be of wide validity in molecules. The total *eigenfunction* of a system,

in terms of the space co-ordinates of the spins of the electrons and nuclei, must change sign whenever any two electrons are interchanged and likewise when any two protons are interchanged.

The case of hydrogen is particularly interesting because the theoretical considerations have recently received striking confirmation from another direction. Owing to the minute perturbations between the nuclei, calculations show that the interchange between the symmetrical set and the antisymmetrical set is of the order of a month. (If there were no perturbation, the two sets would never interchange and hydrogen would consist of two sets of independent components.) This means, that experiments on hydrogen which begin at ordinary temperature are really carried out on a mixture of proportions, 3 : 1. Calculations of its specific heat on this basis are found in complete accord with fact (Dennison). At absolute zero there is no rotation, so that *all* molecules must have antisymmetrical spins, and hydrogen which has been kept at very low temperatures for a long enough time and then heated should have a different specific heat curve from that carried out on normal hydrogen. This experiment has been carried out by Bonhoeffer and Harteck with results in accord with theory.

The relationship between nuclear spin and alternating intensities is discussed by Mulliken (Part I.). The alternating intensities observed in the Raman effect are in complete agreement with those of band spectra and in accord with theoretical expectations except in the case of nitrogen. Rasetti found that transitions between the even levels of the ground state are more intense than those between the odd levels. As nitrogen in the ground state is $^1\Sigma$ like H_2, and from the constitution of the nuclei would be expected to have a nuclear spin like that of hydrogen, this result seems to be in conflict with the rules given above.

Whenever nuclei are unequal, all the rotational levels are theoretically possible and are actually found in heteropolar molecules. Moreover, when the nuclei of homopolar molecules consist of different isotopes as in O^{16} O^{17}, or Cl^{35} Cl^{37}, all the rotational levels are found to occur.

The study of band spectra may thus provide a valuable method of detecting isotopes. The rapid advances which have been made in this field during the last year are summarised by R. T. Birge. Already it has been established that there are oxygen isotopes of mass 17 and 18, and that carbon has an isotope of mass 13. It may be that *all* elements have isotopes, although the agreement of Aston's mass determinations with the usual chemical atomic weights proves that any isotopes as yet unknown can only be present in very small amounts. For the detection of such faint isotopes, the analysis of band spectra seems superior to the mass spectrograph, though, as band spectra give only *relative* masses of two isotopes, the two methods must be used to supplement each other. The indication of band spectra is that O^{16} is 1250 times that of O^{18} and 10,000 times that of O^{17}.

As the mass of the nucleus enters into equations of vibrational and rotational terms, the presence of isotopes can also be detected by the multiplication of the lines in the infra-red absorption spectra (*cf.* "Molecular Spectra of Gases," 1927). The $1{\cdot}76\mu$ band of HCl measured by Imes and elucidated by Loomis provides the classical case, and numerous other cases are given in the papers in Part III.

The use of the isotope effect in the numeration of band systems and in the location of point of origin (vibrational quantum number, $n = 0$) was emphasised by Mulliken in his work on BO, a heteropolar

molecule. Patkowski and Curtis (Part I.) in an investigation into the absorption spectrum of ICl show that the isotopic effect can be used also in homopolar molecules to decide the numeration of the vibrational bands and fundamental vibration frequencies. The work shows the vibrational quantum numbers to be half integral as in all other observed cases and in accord with wave mechanics.

5. The Formation of Molecules.

As recent advances in ultra-violet, visible and infra-molecular spectra are dealt with in special introductions, they need not be further considered in the more general introduction. There are, however, one or two kindred subjects not so specially treated, which come under the general heading of the discussion and which have recently made rapid progress.

A problem of the greatest importance to the chemist is that of molecular formation and dissociation. A complete solution of this problem must indicate the exact conditions under which atoms will combine to form molecules, and this necessarily involves as well a solution of the converse problem, as to what are the states of the products of dissociation. The problem may be stated in the following general form. If two or more atoms in given states (that is, of prescribed term character and multiplicity) approach to form a molecule, (i) what are the molecular states which are possible, and (ii) what are the relative energies of these possible states? The answer to the second question necessarily includes the information as to which molecular states are stable and correspond to molecular binding and which are unstable and correspond to repulsion.

The answer to the first part of the problem has been considered by London [3] for two unlike atoms in S-states, who has found all the molecular terms which are possible according to the theory of groups. The method can be extended to other states (P, D . . .) but not to two like atoms. The latter problem has, however, recently been considered by Wigner and Witmer [4] by methods of the group theory, who have found all the terms which are theoretically possible. For instance, if two F atoms in ^2P states approach to form a molecule, it is possible to have three Σ states, two Π states and one Δ state; and further, each can be a singlet or a triplet. The method does not indicate which of these states correspond to a stable F_2 molecule, but it limits the possibilities. Questions of energy are not considered.

On the other hand, Heitler and London [5] have shown how the interaction of two atoms in homopolar binding may be considered *energetically*, though, as yet, it has been possible to apply the method quantitatively only to the ground state and one or two excited states of the hydrogen molecule. The underlying idea of this work is similar to that of Heisenberg's treatment of resonance in atoms, already referred to. When two hydrogen atoms are far apart, that state in which an electron 1 is considered as belonging to a nucleus a and electron 2 to a nucleus b, has exactly the same energy as the state in which electron 1 belongs to nucleus b and electron 2 to nucleus a. There are thus two *eigenfunctions* with the same energy. On the introduction of a perturbation (*viz.*, that provided by an interaction of the electrons on each other and by

[3] *Z. Physik*, (1928), **50**, 24. [4] *Ibid.*, **51**, 859.
[5] *Ibid.*, (1927), 44, 455.

the nuclei on the electrons), the degeneracy is removed and two energy levels appear. One of these is less than that of the separated atoms and therefore gives binding, the second is higher and leads to repulsion. The lower level is the ground level of the hydrogen molecule. Similar methods have been used by Hylleras and Ludloff to consider the interaction of a normal hydrogen atom and an excited hydrogen atom, and have thus led to a quantitative treatment of the excited states of the hydrogen molecule.

The *eigenfunction* which leads to binding in each case is found to be symmetrical in the space co-ordinates of the electrons (that is, if the co-ordinates of the two electrons are interchanged wherever they appear, the *eigenfunction* remains unchanged). If, therefore, the electrons are assumed to have opposite spin, the complete *eigenfunction* (including space-co-ordinates and spin co-ordinates) is antisymmetrical, and has thus the same property as the *eigenfunctions* of all *atomic* states. On the other hand, the *eigenfunctions* which lead to repulsion correspond to electrons of *like* spin.

London [6] has used this result as a basis to extend the theory qualitatively to more complicated atoms. The guiding principle is that the complete *eigenfunction* for a molecule, like that of an atom, must be antisymmetrical in any two electrons, with a further restriction imposed by the Pauli Principle: not more than two electrons must have the same spacial quantum numbers, or in the language of *eigenfunctions*, not more than two electrons must be *symmetrical* in the *space co-ordinates*.

This principle is fundamental to the whole theory. It is only possible to form a molecule from two atoms when a new pair (or pairs) of electrons can be made symmetrical in the space co-ordinates. This requires that there must be at least one electron in each atom which is not paired already. In order that two such electrons may be "paired," they must have opposite spins.

The Lewis theory of valency arising from uncompleted shells is thus completely confirmed in a quantum mechanical sense. The valency of an atom is equal to the number of electrons in incomplete groups all possessing the same spin. But the number of outer electrons possessing the same spin also determines the multiplicity of the corresponding atomic term. Thus the nitrogen atom in its ground level has three outer electrons with the same spin and its ground term is a quartet (^4S). In general, the multiplicity of an atomic term is one more than the number of unpaired spins. Conversely, the valency of an atom is one less than that of its multiplicity.

All the results, which follow from the Lewis hypothesis, also follow from the new point of view and qualitatively one is as good as the other. The new theory has, however, wider possibilities as it provides a possible method of dealing quantitatively with chemical binding. Moreover, it links up ideas of valency with the spectroscopic evidence of multiplicity.

The various valency numbers which an element may have are easily explained in terms of electron spin. Carbon may be quoted as an example. Carbon in the normal state has two electrons in the $1s$ levels (closed group), two electrons in the $2s$ level (closed group), and two electrons in different $2p$ states with the same electron spin (spectroscopic term ^3P). The normal carbon atom has two valencies. If, however, the carbon is excited so that three electrons occupy three different $2p$ states, with only one electron in the $2s$ state, then these four outer

[6] *Z. Physik*, (1928), **46**, 457.

electrons may all have the same spin, and the atoms thus become tetrahedral.

As pointed out in the opening paragraph, the multiplicity of *molecular* terms is also determined by electron spin, so that molecular spectra provide valuable information about the valency bonds in a molecule. The ground state of O_2 is found to be a triplet ($^3\Sigma$). As the oxygen atom in its normal state is also a triplet (^3P), and thus has two uncoupled electron spins, the inference is that only one electron from each atom is paired in O_2.

A valuable experimental method of relating the various states of a molecule with the products of dissociation is that of dissociation by light absorption, initiated by Franck [7]. The characteristic feature of the absorption spectrum is that the vibration bands converge to a limiting frequency followed by a continuous spectrum. The accepted explanation is that absorption produces in the first place a change in the electronic configuration, without changing the internuclear distance. If the equilibrium distance of the nuclei in the new configuration is greater than the old, the atoms in swinging from the old to the new may gain sufficient energy to produce dissociation. The convergence limit of the vibration band indicates the energy which is just necessary to produce dissociation. When the convergence of the band is not observed, other methods have been devised to estimate the point of convergence.

An improved method is now suggested by R. T. Birge (p.). The essential point of the paper refers to a new method of plotting the frequency of vibration, which, it is claimed, leads to more trustworthy values of the heat of dissociation.

Ellis (p.) employs the methods of Birge and Sponer to calculate the heats of dissociation of C—H and N—H groups in organic compounds. The results are in agreement with thermal data and indicate that the heats of dissociation of these groups are dependent on chemical constitution.

The band spectra of polyatomic molecules show a more gradual transition from band to continuous spectra. The bands often become *diffuse* before passing into a continuous spectrum. These diffuse bands are attributed to a loss of rotational quantisation. V. Henri employs the term " predissociation " to indicate the state of the molecule after receiving energy corresponding to the frequencies of these diffuse bands, and brings forward evidence to show that in this state the molecule is photochemically active.

Goodeve and Stein (Part I.) find that the vibration bands of chlorine dioxide become diffuse at the fourteenth level, beyond which there is a change in separation of the bands. This points to a change in molecular configuration and suggests a close connection with the work of Henri on predissociation.

In most cases, it has been found that an excited molecule dissociates into one normal and one excited atom. This is easily decided from energy considerations, when the spectrum of the component atoms is known, as it usually is. On the other hand, a normal molecule usually dissociates into two normal atoms. Recently a new result of considerable importance has been found by Herzberg [8] and interpreted by Heitler and himself.[9] It appears that some molecules dissociate from the ground state into one *normal* and one *excited* component; whereas

[7] *Trans. Far. Soc.*, (1925), **21**, Part III.
[8] *Ann. Physik*, (1928), **86**, 189. [9] *Z. Physik*, (1929), **53**, 52.

an excited state dissociates into two normal components. It follows that on combination one of the atoms must be activated before a normal molecule can be formed. Examples of this type are CN, BO, SiN, N^+_2, and $(CO)^+$. These results are in accordance with the theory of binding outlined above. Normal C is divalent and can therefore only use up two of the possible valencies in N. Excited C on the other hand is tetravalent and so is able to produce a stronger binding with N.

Other cases where a normal molecule separates into excited atoms are given by Bengtsson and Hulthén, who find, for instance, that CuH separates from its normal $^1\Sigma$ state into an excited Cu atom ($^2D'$ state) and an H atom in a $3d$ level.

Formation of Molecules from Atoms.

The formation of a homopolar molecule AB from the atoms A and B is a very rare event; this is shown experimentally by the stability of hydrogen and nitrogen atoms, and by the work of Bodenstein on the recombination of bromine atoms. Beutler and Polanyi also conclude that the formation of heteropolar molecules is subject to the same difficulty. The difference of energy between two *normal* atoms A + B and a *normal* molecule AB is not necessarily the energy of dissociation. The excess of energy on molecule formation must be dissipated either by molecular collision or as radiation. Thus the recombination of atoms depends largely on triple collisions or on the possibility of the emission of radiation. Kondratjew and Leipunsky (Part I.), from a study of the thermoluminescence spectra of the halogens, conclude that the continuous spectrum observed is due to the emission of radiation on the combination of atoms. They find that the process

$$Br + Br' \rightarrow Br_2 + h\nu$$

is very rare.

Some molecules dissociate not into atoms, but into ions. These are said to be heteropolar molecules, and to have polar binding. It has been found that the distinction between homopolar binding and heteropolar binding is not a sharp one, and it is sometimes difficult to decide into which class a molecule is to be placed. HCl was long thought to be a polar compound but is now regarded as homopolar.

It may be said that the type of binding is in all cases a question of energy. If the energy required to ionise an atom (say, an alkali atom) and to transfer the electron to another atom (say, a halogen) is small, then the work done is more than compensated for by the gain of potential energy as the ions move together under the electrostatic field. In such cases, the system has less energy as a polar compound than as a non-polar structure. In KCl, for example, only half a volt is required to transfer the electron from the alkali to the halogen, and this energy is soon gained by the Coulomb attraction. On the other hand, about 10 volts are required for a similar process in HCl.

Hund (Part I.) examines the London theory from the point of view of energy changes in molecular formation and suggests possible criteria for the formation of molecules. The characteristic difference between H_2 and HeH may be due to (1) the fact that in H_2, as in helium, the two electrons are in equivalent levels, whereas that is impossible in HeH, owing to the fact that two of the three electrons are already in equivalent levels; (2) the splitting up of the H + H term and the absence of any splitting in the case of He + H term.

A further method which Hund has used with success to determine whether molecular formation is possible or not is to consider the sum of the energy levels of the separated atoms and then to compare them with the levels of a "united atom" containing the same number of electrons. The system He + He passes over to the Be atom, but the energy of Be is much higher than (He + He), and Hund considers this as an indication of repulsion as the He atoms are pushed together. The formation of a He_2 molecule from two normal He atoms is then not possible. On the other hand, the Li + H system, which also passes to the united atom Be, has a higher energy than the Be, owing to the small ionisation potential of Li. The intermediate system of LiH is therefore a possible one. Hund has used the same method to interpret more complicated molecular spectra, as of CN, for example, which is intermediate between the C + N and Al systems. There are difficulties, however, in this method; in particular, it indicates that a normal C and a normal N atom lead to a normal CN molecule, which Heitler and Herzberg have shown not to be the case.

6. The Raman Effect.

The light scattered when a beam of monochromatic radiation passes through gaseous, liquid, or crystalline media has been resolved into (1) radiation with the same frequency N as the incident light; (2) a series of bands of frequency $N \pm n$, and (3) a continuous spectrum which may be 50 Å. wide. (*Cf.* Cabannes, Part II.).

The values of n are found in many cases to agree with the frequencies of infra-red bands and this implies that the Raman lines are due to interchanges between the energy of the incident radiation and the vibrational and rotational energies of the molecules of the medium. The negative bands $(N - n)$, which are more intense than the positive bands $(N + n)$, may be regarded as due to the retention of energy from the incident radiation in the form of molecular rotational and vibrational energy. The positive bands, on the other hand, are due to an augmentation of the energy of the radiation at the expense of intermolecular energy.

Professor Raman in his summary gives the essential features of the phenomena, and, in particular, refers to the strong polarisation of the radiations scattered with altered wave-lengths, and to the incoherent nature of these radiations. An interesting field of study is opened up by the comparison of the Raman lines with those of infra-red spectra. For the molecular spectra give us information about those molecular states which are optically active. It is only in special cases that the optically inactive states can be detected. One of the most important features of the Raman effect is that it has corroborated speculation as to the existence of inactive states. One need only mention the fundamental vibrations of CO_3'' in crystalline carbonates investigated by Schaefer (Part III.), and of gaseous carbon dioxide.[10] Inactive fundamentals are represented in the infra-red absorption spectra only in combination with other vibrations, but they always appear in great strength in the Raman effect. Similarly the optically inactive vibrations of nitrogen, hydrogen, and oxygen molecules, are represented by Raman lines (McLennan and McLeod).

Of parallel importance is the deduction of the relative *weights* of

[10] *Cf.* Rasetti, *Nature*, 1929, **123**, 205.

rotation levels from the Raman lines. These serve to confirm, and, in some cases, to supplement the results obtained from molecular spectra in the visible and ultra-violet. Thus, McLennan (Part II.) finds in ordinary liquid hydrogen the two rotational transitions $0 \rightarrow 2$ and $1 \rightarrow 3$, the latter being the stronger. The relative intensities are explained if the odd rotational levels have three times the weight of the even levels, a result in agreement with that deduced from the specific heat of hydrogen gas. Rasetti finds alternating intensities of the expected type both in gaseous hydrogen and gaseous oxygen, but in nitrogen, transitions between even rotational levels are stronger than those between odd levels. Band spectra data are lacking in this case. This latter result of Rasetti constitutes a serious difficulty, as yet unexplained, for nitrogen in the ground state is $^1\Sigma$ like hydrogen, and from the constitution of the nuclei would be expected to have a nuclear spin like that of hydrogen.

In the spectra of crystalline media, we have a means of completing the information yielded by X-ray researches, a point which is made by both Schaefer and Cabannes. The Raman spectra from crystals are important in that they enable studies to be made of the scattering of light from molecular groupings whose approximate orientations are known from X-ray measurements. Cabannes (Part II.) has shown the value of measurements of the intensities and polarisation of the Raman lines in this connection.

Comparison of the Raman spectra of liquids and gases has been shown by Daure (Part II.) to be of importance in the study of the association of liquids. He deduces the presence of $NH_3 - NH_3$ in liquid ammonia by this means.

7. Structure of Polyatomic Molecules.

The structure of polyatomic molecules and the nature of the nuclear spins and rotations can be derived from a study of spectra. The main features of the configurations of normal molecules can be derived from infra-red spectra and those of excited molecules from the fine structure of optical and ultra-violet spectra.

For diatomic molecules, the moment of inertia I, and the distance between the nuclei can be obtained from the equation $\Delta\nu = hK/4\pi^2 I$, where $\Delta\nu$ gives the frequency differences of the rotational spectrum and K is an integer. Also the differences between the frequency maxima in the rotation-vibration spectra gives the same information. For diatomic molecules the two principal moments of inertia are equal and the third about the axis joining the two nuclei is negligible. Polyatomic molecules which are linear or nearly so give very similar spectra to those of diatomic molecules (*cf.* Barker and Meyer, Part III., for a classification of polyatomic molecules into types).

Where there is more than one moment of inertia as in ammonia, the relationship between the moments of inertia and the various quantum numbers is more complex, but can be derived by the application of quantum mechanics.[11] The fine structure of a vibration band depends on the direction of vibration of the electric moment; thus bands due to vibration along different axes show different rotational frequency intervals. Where the axes of rotation, and the moments of inertia are known, the arrangements of the atoms in space and their distances apart can be determined.

[11] *Cf.* Colby, "Molecular Spectra of Gases," 1926, 59; Dennison, *Phil. Mag.*, 1926, **1**, 1925; Reich and Rademacher, *Z. Physik*, 1928, **39**, 444.

In the last few years there has been a rapid advance in our knowledge of the rotational and vibrational levels of molecules in the unexcited state. The study of infra-red absorption spectra has revealed not only the magnitude of internuclear distances and the nature of structural arrangements in space, but also has yielded precise information about the rotational and precessional movements of molecules. Detailed knowledge is at present limited to simple molecules in the gaseous state. For complex organic molecules, studied in the solid or liquid state, only the vibrational levels have been systematically examined, and the manner in which the frequency of these levels changes with modification in chemical constitution. In an introductory address on the infra-red spectra of gases, Sir Robert Robertson outlines the advances so far made, especially with reference to its bearing on chemical problems.

E. F. Barker and C. F. Meyer, in a survey of the experimental investigations on the vibration bands of simple molecules in the gaseous state, proposes a method of classification of molecules into groups according to the complexity of the rotational levels. Diatomic and linear molecules like carbon dioxide and acetylene only rotate in a plane and show no precession. Methane, on account of its symmetry, can rotate about any axis without precession, but, in general, polyatomic molecules rotate with a precession, the complexity of which depends on the molecular symmetry. Ammonia, ethane, methyl fluoride, etc., which have symmetry about one axis of rotation, give a less complex rotational structure than water, sulphuretted hydrogen, and ethylene, which possess three unequal moments of inertia. It is a curious fact that carbon dioxide is linear, while water is a triangular molecule.

Rawlins (Part III.) summarises the evidence from the infra-red bands and measurements of electric moment of carbon dioxide with a view to the elucidation of its structure. In agreement with Barker and Meyer, he concludes that this molecule is linear.

Organic Molecules.—There was an early recognition by organic chemists of the fact that the characteristic absorption spectra of organic molecules was caused by the presence of certain chromophoric groups of atoms in the molecule; and this recognition has played no small part in the development of organic chemistry. It is possible nowadays, with greater precision, to refer a particular absorption band to a single linking in an organic molecule. The characteristic vibrations of the ground states of the C — H, C = O, C ≡ N, C — OH, N — H linkings have all been recognised (due to the work of Bonino, Lecomte, Ellis, Sallant, and others, on the infra-red spectra). The effect of chemical constitution on the frequency of these characteristic vibrations has been examined (*cf.* Bonino, Part III.), especially in the case of the C—H linking. The effect of lengthening the carbon chain, of the presence of the double carbon linking, of ring formation, and the influence of hydroxyl and halogen substitution shows that the wave-length of the characteristic band depends slightly on the nature of the groups to which C—H is attached (3·25 — 3·5μ). Thus the C—H spectrum for a complex organic molecule is composed of a series of bands, the number of which depends on the number of such linkings in the molecule. The separation of these bands has been partially effected by Bonino and Petrakaln in the case of the Raman spectra, and Wood, in a contribution to the present discussion, records the separation of the 3·4μ band into a fine structure which varies in character from compound to compound.

From the characteristic frequencies, calculations can be made re-

garding the binding force between the atoms in the molecule, and these compared with the ease with which chemical substitutions occurs.[12] Rapid progress in this direction can only be secured by the employment of the maximum dispersion attainable.

8. Experimental Technique.

The development of experimental technique has accompanied the growth of theory. The requirement of still higher dispersion is being met by the introduction of new types of spectrometric arrangement, larger gratings, etc., and the introduction of time-saving devices (*e.g.* automatic registration of infra-red spectra). (*Cf.* Barker and Meyer for development of technique in infra-red.) Measurements of Raman spectra provide a means of determining vibration and rotation spectra, which gives narrower lines than those obtained by the usual infra-red methods and determination of frequency can be made with greater precision. The technique of the study of this effect is improving very rapidly (*cf.* Wood, who recommends the employment of a helium tube for excitation of Raman lines). A further important advance is the applicaton of the methods used in the visible region to the measurement of the vibration levels of the ground states of polyatomic molecules (*cf.* Mecke and Ellis, Part III.).

The introduction of wave mechanics has so unified the various branches of spectroscopy that it is difficult to foresee the extent of their usefulness, and particularly in relation to chemistry, but the experience of the last decade has taught us that chemical change is accompanied by electronic transitions, and hence we must look mainly to spectroscopy in the visible and ultra-violet for the development of theories of chemical change and for advances in our knowledge of valency. On the other hand, structural chemistry and, in particular, knowledge of the structure of organic molecules is likely to be advanced principally by studies in the infra-red region.

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PART I. BAND SPECTRA IN THE VISIBLE AND ULTRA-VIOLET REGIONS.

NOMENCLATURE AND SYMBOLISM FOR THE SPECTRA OF DIATOMIC MOLECULES.

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The main lines of the theory of band spectra, at least so far as diatomic molecules are concerned, seem now sufficiently well established to enable a system of notation to be constructed which offers a good chance of a reasonable degree of permanence. There are too many existing notations and they are usually of an inconvenient character, for example, too many suffixes and sub-suffixes are used. The main points to be aimed at are (1) compactness, subject to the necessary information being accurately expressed; (2) simplification; and (3) to keep as close as possible in corresponding things to the existing notation for line spectra which has received a fairly general acceptance.

The views which I am presenting are essentially those of Mulliken who has discussed the matter with Hund and others. The matter seemed to me to be one which might very profitably be considered by a conference of this kind. Whilst the scheme appears to me to be satisfactory, it is not being put forward as final and some of those present may be able to suggest improvements.

It is hardly necessary to recall to this assembly that the term values (energy levels) of these spectra can be expressed as $E/hc = F = F^{el} + F^{v} + F^{r}$ where F^{r} measures the rotational, F^{v} the vibrational, and F^{el} the electronic energy. Strictly the terms involve some interplay between these different types of energy, but this linear combination is a satisfactory approximation for the basis of classification. The notations required for the expression of F^{v} and F^{r} are comparatively simple; it is in the electronic term that the complexity arises. We now have a good deal of information about these terms; in H_2 about 40 different electronic levels are known and in He_2 the number is still higher. The way in which these levels intercombine is known. In each spectrum there are 4 sets of non-intercombining electronic levels, one pair corresponding to the parhelium and the other to the orthohelium line spectrum. In both spectra series are known which obey a Rydberg formula. In He_2 the fine structure multiplicity of the orthohelium-like bands is now experimentally established. In the bands of various molecules the electronic multiplicity can be calculated by adding up the spins of the electrons which make up the molecules in the same way as the multiplicities of line multiplets can be computed from the spins of the electrons making up the atom. In general we can say that the properties of the electronic terms of molecules can be constructed to a very large extent from a knowledge of the quantum states of the electrons in the molecules concerned. Our notation will

evidently have to embrace all, or most of, the complications met with in line spectra.

In general it will be more complicated. We can regard the emitting electron of a molecule alternatively either as an electron of one of the constituent atoms perturbed by the other atom or that of an atom, containing as many electrons as the total number in the molecule, perturbed by the split nucleus. In either case we have a Stark effect for a field along the internuclear axis; so that we can expect as many terms as in the Stark effect in a line spectrum. The total "azimuthal" quantum number may be space-quantized to this axis. This enables transitions to occur such as $S \rightarrow S$ which would be forbidden in line spectra. Again the coupling between this quantum number and the internuclear axis may depend on the speed of rotation. This may have a very profound effect on the rotational structure of bands and may abolish the usual rotational constants. Extreme examples of this are shown in the spectrum of H_2.

I. Quantum Numbers.

I shall now enumerate the *Quantum Numbers* which it is necessary to employ in order to account for these and other phenomena exhibited by diatomic spectra, using the proposed notation. For *Individual Electrons* we use the lower case letters. This conforms with the usage for line spectra. There seems much to gain and nothing to lose by this. Thus:

n = principal quantum number.
l = azimuthal or analogous quantum number (*i.e.* $l = n_\theta + n_\phi$ for spherical co-ordinates, as in atoms, or $l = n_\eta + n_\phi$ for elliptical co-ordinates, as in H_2+).
s = spin quantum number $= \frac{1}{2}$.
λ = quantum number representing the projection of l on the molecular axis, with the direction of Λ (see below) taken as the positive axis.

n l s represent essentially the same things as the corresponding letters when used in line spectra. λ is introduced to recall the close connection of this symbol with l. λ was formerly i_{l_τ} or σ_{k_τ} or σ_{l_τ}; the abolition of such symbols as these is very desirable. If quantum numbers for several electrons 1, 2, 3, . . . are to be designated, subscripts can be used, as l_1, l_2, l_3 . . . λ_1, λ_2, λ_3. . . .

For the *Molecule* as a whole we may require for the *Electronic Configuration*:—

L = resultant of the l's.
S = resultant spin.
J^{el} = resultant of L and S.
Λ = resultant orbital angular momentum around molecular axis.
$= \Sigma\lambda$ if the individual λ's exist, or
= projection of L on the molecular axis, if L exists.
X = projection of S on the molecular axis defined so that X has positive values when it is parallel to L.
Ω = resultant of Λ and X.
= projection of J^{el} on the molecular axis, if J^{el} exists.

The existing notation which these would abolish is :—

$$i \text{ or } \sigma = \Omega.$$
$$l_s \text{ or } \sigma_s = X.$$
$$i_l \text{ or } \sigma_k \text{ or } \sigma_l = \Lambda.$$

L, and especially J^{el}, usually do not exist for molecules, but it is sometimes useful to define L in terms of the atom obtained by uniting the nuclei. X does not exist for $\Lambda = 0$.

For the molecule as a whole we also use :

n = vibrational quantum number.
J = quantum number of the final resultant angular momentum.
M = magnetic quantum number.
= projection of J on the axis of the external field.
$\frac{Nh}{2\pi}$ = angular momentum of the nuclei (N is not a quantum number).

n has already been used for the principal quantum number of individual electrons, but it is well established in both connections and the double usage does not seem to lead to much difficulty. If J (in the form j) were less well established it would be preferable to adopt a new symbol to avoid conflict with the atomic J (here called J^{el}). J^{el} is, however, seldom needed.

The relative importance of these different quantum numbers and the nature of the connections between them depend on the comparative magnitudes of the interactions between the different types of energy in the molecule. The recognition of this is due to Hund (*Z. Physik*, **36,** 657 (1926)), who pointed out the important types of interaction to be expected. These are :

(1) The interaction of the l and s of the individual electrons.
(2) The influence of the unique axis due to the presence of 2 nuclei in perturbing the motion which would otherwise be determined by the l (or L) alone.
(3) The interaction of the L and S.
(4) The effect of L on the rotation by altering the moment of inertia.

Various cases arise depending on the relative magnitudes of these 4 factors. The connections between the different types of quantum numbers are in general different for the different cases. The cases which seemed to be of most theoretical interest have been classified and discussed by Hund. These cases are specified below and the specification is followed by a shorthand description of the behaviour of the various quantum numbers. In this shorthand all sums are vector sums and arrows ($\rightarrow$) indicate projection on an axis.

Specification.	Behaviour.
Case (*a*) (2) > (3) and (4).	$(L\rightarrow)\ \Lambda$ and $(S\rightarrow)X$, $\Lambda + X = \Omega$, $\Omega + N = J$, $(J\rightarrow)\ M$.
Case (*b*) (2) > (3) and (4).	$(L\rightarrow)\ \Lambda$, $\Lambda + N = K$, $K + S = J$ (for weak fields), or $(L\rightarrow)\ \Lambda$, $\Lambda + N = K$, $K \rightarrow M_k$ and $S \rightarrow M_s$, $M = M_k + M_s$ for strong fields.
Case (*c*) (1) > (3) > (2) > (4).	$L + S = J^{el}$, $J^{el} \rightarrow \Omega$, $\Omega + N = J$, $J \rightarrow M$.

Specification.	Behaviour.
Case (*d*) (1) > (4) > (2) > (3).	Let R = quantum number of nuclear rotation (Hund's p_r) $R + L = K$, $K + S = J$, $J \rightarrow M$ for weak fields, or $K \rightarrow M_k$, $S \rightarrow M_s$, $M_k + M_s = M$ for strong fields.

Cases *a* and *b* are incompletely specified in this table. In both cases Λ is constant and quantized. In case (*a*) the interaction between Λ and X is strong compared with the effect of the rotation (which tends to disorganise them), so that they remain coupled together along the axis. In case (*b*) this interaction is weak compared to the effect of rotation, so that the spin is no longer coupled to the axis. Case (*a*) will generally apply to states of low rotational energy. In case (*b*) if $S = 0$ or if the coupling of K and S is negligible so that J does not exist, as in H_2 and He_2, K is the important rotational quantum number. For $S = 0$ either K or J might be used, but it would seem preferable to use K, especially since, for example in H_2, it may not always be certain whether $S = 0$ or 1.

Case (*c*) is not, as yet, known to occur. In case (*d*) if $S = 0$ or the coupling of K and S is negligible so that J does not exist, as in H_2 and He_2, K and R are the important rotational quantum numbers.

II. Configuration and Term Symbols.

For *Individual Electrons* the notation proposed to be used is as in the following examples :—

$ns\sigma$	for an electron with	principal	quantum	number	$n, l = 0, \lambda = 0$
$np\sigma$	,,	,,	,,	,,	$n, l = 1, \lambda = 0$
$np\pi$	,,	,,	,,	,,	$n, l = 1, \lambda = 1$

and so on, using s, p, d, f, g, h for $l = 0, 1, 2, 3 \ldots$, and using σ, π, δ, ϕ, γ, η . . . for $\lambda = 0, 1, 2, 3, \ldots$

For *Electron Configurations* as in the following example: $1s\sigma^2\ 2s\sigma^2\ 2p\sigma^2\ 2p\pi^3\ 3d\pi$ where the index after the Greek letter denotes the number of individual electrons in the state specified. If the n values are unknown, or well known, this may be abbreviated to $\sigma^2\ \sigma^2\ \sigma^2\ \pi^3\ \pi$ or still further, if desirable, to $\sigma^6\ \pi^4$.

For *Molecular States.*—If Hund's cases (*a*) or (*b*) are approximately realised use Σ, Π, Δ, Φ, Γ, H . . ., to indicate $\Lambda = 0, 1, 2, 3, 4, 5 \ldots$. Also use S, P, D, F . . . if desired to indicate $L = 0, 1, 2, 3, \ldots$ if an L value for the molecule, or for the atom obtained by uniting the nuclei, can be assigned. To indicate both L and Λ, symbols such as $P\Sigma$, $\Delta\Pi$, etc. should be used.

Indicate multiplicity as in atoms, *e.g.*, $^1\Sigma$, $^2\Pi$, $^3D\Sigma$, etc.

If Hund's case (*a*) is approximately realised, use final subscripts to denote the value of $\Lambda + X$ (for singlet states no subscript is needed; for Σ states with $S > 0$, no subscript is possible, since X does not exist).

Examples $^1\Sigma$, $^1\Pi$, $^2\Sigma$, $^3\Delta_1$, $^4\Pi_{2\frac{1}{2}}$, $^4\Pi_{1\frac{1}{2}}$, $^4\Pi_{\frac{1}{2}}$, $^4\Pi_{-\frac{1}{2}}$, etc.

For the even and odd terms of homopolar molecules which indicate the symmetry properties with respect to an interchange of nuclei, use a superscript ^{0} or ^{e} on the right of the term symbol, as $^3\Sigma^0$, $^1\Sigma^e$ or $^2\Pi_{\frac{1}{2}}{}^0$. ^{0} means $\Sigma l =$ odd and ^{e} means $\Sigma l =$ even.

Vibrational quantum numbers, n, and K or J values in connection

with electronic terms should be indicated as in the following examples : ${}^3\Sigma^0(n, K)$, ${}^2\Pi^e_{1\frac{1}{2}}(n, J)$, etc.

Perhaps the question of notations for positive and negative terms and A and B (or a and b) sublevels in Λ type doubling, formerly called σ type doubling, might be left over for the present.

For *Term Values* in general we retain the symbol F, as in $E/hc = F = F^{el} + F^v + F^r$. Intervals of term values, obtained empirically, might be designated as in the following examples :
$\Delta F^v(n_1, n_2)$, $\Delta F(J_1, J_2)$ or $\Delta F^r(J_1, J_2)$, where n_1 and n_2 or J_1 and J_2 are two values of a quantum number, all other quantum numbers being kept fixed.

III. Branches in Bands.

For branches corresponding to $J' = J'' - 2$, $J' = J'' - 1$, $J' = J''$, $J' = J'' + 1$ and $J' = J'' + 2$ the letters O, P, Q, R and S respectively are suggested. The designations O and S would be useful in the Raman effect.

IV. Symbols for Important Molecular Constants.

Mulliken suggests the use of the following symbols to remove the ambiguity in the use of certain symbols arising out of the discovery that the vibrational energy of a molecule is not zero when the vibrational quantum number becomes zero :

r_e = equilibrium value of the distance between the nuclei.
$I_e = \mu r_e^2$.
$B_e = h/8\pi c\mu r_e^2$.
$B_n = B_e - \alpha(n + \frac{1}{2}) = B_0 - \alpha n$ (B_e is the equilibrium value of B, B_0 its value for $n = 0$).
$c\omega_e$ = vibrational frequency for infinitesimal amplitude, ω_e being in cm^{-1}. ($c\omega_n$ can now be used for the vibration frequency for the nth state of vibration; in particular $c\omega_0$ is the frequency for $n = 0$).
$D_e = 4B_e^3/\omega_e^2$ = coefficient of J^4.
$D_n = D_e + \beta(n + \frac{1}{2}) = D_0 + \beta n$,

and so on.

I append the following remarks on this notation which I have received from Professor Mulliken who is, unfortunately, not able to be present :—

The most important new suggestions made above are in regard to the use of λ, Λ, X, Ω, K, R, J, M. Λ and λ correspond to a translation into Greek of L and l; the relation between L and Λ is the same as that between the term-symbols S, P, D, F . . . used for atoms (and sometimes also for molecules) and the term symbols Σ, Π, Δ, Φ . . . used for molecules (*cf.* next section); similarly, just as we have L for the atom and l for individual electrons, with symbols S, P, D . . . and s, p, d . . . to correspond, so we now have Λ for the molecule and λ for the individual electrons, with term-symbols Σ, Π, Δ . . . and σ, π, δ . . . to designate the values of Λ and λ respectively. The choice of Λ and λ was governed both by the analogy above-mentioned (L, l, S, P, D . . . s, p, d . . . Λ, λ, Σ, Π, Δ, . . . σ, π, δ . . .) and by the fact that Λ and λ are simple unambiguous symbols not already in common use as quantum numbers, and far preferable to such cumber-

some symbols as i_l, $i_{l\tau}$, σ_l, $\sigma_{l\tau}$, or the like. The use of both capital and small letters is also particularly valuable here, just as in the case of L and l in atoms.

The choice of Λ for the component of orbital electronic angular momentum along the figure axis makes it very desirable for consistency to use other Greek letters for the components of spin and of total electronic angular momentum along this axis. [Wigner and Witmer used η and ι respectively (also λ where we are using Λ), but these symbols in the capital forms (H and I) which are now needed for consistency with the use of capitals for all angular momenta associated with the molecule as a whole, do not seem very suitable; among other objections I is likely to be confused with the symbol I frequently used in band spectra to denote moment of inertia.] An examination of the Greek alphabet discloses no particularly suitable symbols not already in use, or not identical in printed form with Latin letters. The choice of X and Ω made here seems to be about the best that can be done, and seems relatively unobjectionable, and preferable to the symbols formerly used (i_s or σ_s and i or σ). [The use of Σ in place of X was at one time suggested (Σ would then be related to S in the same way as Λ to L), but this seems likely to cause too much confusion with Σ as a summation sign and with the use of Σ to denote $\Lambda = 0$.] Neither of the symbols X and Ω is in previous use as a quantum number, and neither is commonly used in the quantum theory in a way likely to cause confusion with their use here. [For individual electrons, χ and ω can be used if needed, in a similar manner to λ, but their use in this way is likely to be rare, especially in the case of ω; for this reason no serious objection can be raised to the existence of such a possible use of ω.] Furthermore, the quantities denoted by X and Ω are at any rate less important and less often needed than that denoted by Λ, so that one can for this reason better tolerate them in spite of objections that may be raised.

The choice of the symbol K was governed by the following considerations: (*a*) K is a quantity which always includes the electronic orbital angular momentum L (or Λ) as a component; (*b*) K is a quantity which when combined with S gives J, and is thus closely analogous to L of atomic spectra. For both reasons it seemed desirable to use a symbol related to L of line spectra. There are strong arguments for using here the symbol L itself, especially since we are suggesting J for the resultant angular momentum of the molecule. But the use of a molecular L different in meaning from the atomic L would cause confusion, especially in cases where the atomic L is also needed (*e.g.* in Hund's case (*d*)); this difficulty could of course be overcome by using L^{el} for the purely electronic L just as we have used J^{el} for the purely electronic J, but the quantity J^{el} is one which seems likely to be much less often used than would L^{el}. Hence, on the whole, it seems best to keep L for the purely electronic L, as in atoms, and to introduce a new symbol for our present purpose. For this K seems espcially acceptable, partly because in atomic spectra K has been used with a meaning similar to that of L, but is no longer so used. Obviously K is preferable to the symbols p_l or j_k hitherto used.

The suggested use of R and K in Hund's case (*d*) perhaps needs no especial comment, except the remark that the choice of suitable symbols here now appears of more importance than formerly, in the light of recent work on He_2 and H_2.

BAND SPECTRA AND ATOMIC NUCLEI.

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Much attention is now being devoted to the problem of nuclear structure. There are two kinds of information which band spectra contribute to this problem, namely, data on nuclear masses and on nuclear "spins." The *isotope effect* in band spectra has served to confirm, and in some cases, notably oxygen, to extend the results obtained with the mass spectrograph. The phenomena of *alternating intensities* and alternate missing lines in band spectra are at present the chief source of our knowledge about protonic and nuclear angular momenta; another source is found in the hyperfine structure of atomic spectrum lines.[1] In addition to information on nuclear masses and angular momenta *per se*, band spectra yield interesting results in regard to the effects of these features on the energy levels and other properties of molecules.

This paper is intended as a review of our present knowledge of alternating intensities and related topics. For a very complete recent discussion of the isotope effect in band spectra, the reader is referred to Mecke's *Bandenspektra und ihre Bedeutung fur die Chemie* (Vol. 20, No. 3 of the series *Fortschritte der Chemie, Physik, und physikalischen Chemie*), and to Professor Birge's paper before the Faraday Society.

In the spectra of molecules which contain two nuclei, equal both in charge and in mass, one finds that in every series of band lines, every other line is relatively weak or else missing. Heisenberg and Hund [2] have suggested that this phenomenon can be explained by assuming that a necessary condition of existence for any state of a molecule is that it be antisymmetrical in all protons as well as in all electrons. Thus, suppose $\psi^k(x_1y_1z_1s_1,\ x_2y_2z_2s_2,\ x_{\mathrm{I}}y_{\mathrm{I}}z_{\mathrm{I}}s_{\mathrm{I}},\ x_{\mathrm{II}}y_{\mathrm{II}}z_{\mathrm{II}}s_{\mathrm{II}}\ \ldots)$ is the complete Schrödinger function of the co-ördinates (x, y, z) and spins (s) of the electrons (indices 1, 2 . . .) and protons (indices I, II . . .) for the kth quantum state of a molecule. Then, if any two electron indices, or any two proton indices, are interchanged wherever they appear in ψ^k, the resulting new function must differ from ψ^k precisely by a factor -1. The correctness of this antisymmetry rule for the extranuclear electrons in atoms is well established by the facts of line spectra. Its applicability to protons is confirmed, as we shall see, by the specific heat [3] and band spectrum data for hydrogen. In the case of molecules with more complex nuclei, there seem, however, to be some difficulties.

Hydrogen Molecule.

Theoretical Considerations.—The simplest molecule which shows phenomena explainable in terms of the proton antisymmetry rule is hydrogen. Here we assume that each ψ^k must be an antisymmetric function

[1] S. Goudsmit and E. Back (*Z. Physik*, **43**, 321, 1927; **47**, 174, 1928) have shown that the Bi nucleus possesses an angular momentum of 9/2 quantum units.

[2] W. Heisenberg, *Z. Physik*, **41**, 261 (1927); F. Hund, *Z. Physik*, **42**, 112 (1927); **51**, 783 (1928).

[3] D. M. Dennison, *Proc. Roy. Soc.*, **115A.**, 483 (1927).

of the arguments of the two electrons (1 and 2), and of the arguments of the two protons (a and b). To a fairly good approximation,[4] any ψ^k can be written as a product of factors as follows:—[5, 6]

$$\psi = [\psi_{el}(x_1 \ldots z_2 x_a \ldots z_b)][\psi_{nuclear}(\Lambda, x_a \ldots z_b)] \\ [\psi_{el}(s_1 s_2)][\psi_{nuclear}(s_a s_b)] \quad . \quad . \quad . \quad (1)$$

The first factor depends on the co-ördinates both of nuclei and of electrons, and is capable of being either symmetric (Sy) or antisymmetric (An) in the electrons, and in the protons; the second and fourth factors can be either Sy or An in the protons only; the third factor can be Sy or An in the electrons only.[7] For brevity, we shall hereafter use SyE, AnE, SyP, AnP, and (later) SyN and AnN to denote Sy or An in electrons, protons, or nuclei, respectively (in the special case of H_2, SyP and AnP are respectively identical with SyN and AnN).

The symmetry properties of the first ψ_{el} factor in equation 1 can be best understood by thinking in terms of an imagined case [8, 9] in which the electrons exert no forces on each other, but move in the field of two fixed centres. In this imagined case (as *actually* in H_2^+),[10] ψ_{el} is strictly separable by the use of elliptical co-ördinates into three factors for each electron:

$$\psi_{el}(x_1 \ldots z_b) = \psi(\xi_1)\psi(\eta_1)\psi(\phi_1)\psi(\xi_2)\psi(\eta_2)\psi(\phi_2) \quad . \quad . \quad . \quad (2)$$

where $\xi = (r_a + r_b)/R$, $\eta = (r_a - r_b)/R$, r_a or r_b being the distance of an electron from proton a or b and R being the distance between the protons (here assumed fixed), while ϕ is the angular co-ördinate of an electron measured, say, counterclockwise, around the line $a \rightarrow b$[11].

Corresponding to the co-ördinates ξ, η, ϕ for each electron in equation 2 are quantum numbers n_ξ, n_η, and n_ϕ. In describing the state of an electron, it is convenient to use as quantum numbers

$$n = n_\xi + n_\eta + n_\phi + 1,\ l = n_\eta + |\, n_\phi \,|\,, \text{and} \lambda = |\, n_\phi \,|\,.$$

The use of n and l is good because, as can be shown by a consideration of the nodal surfaces of $\psi(\xi)$, $\psi(\eta)$, and $\psi(\phi)$, n and l as here defined would

[4] When higher approximations are considered, such a separation into factors is no longer possible, but the changes needed to obtain an accurate expression are never such as to alter the *symmetry properties* in electrons and protons, which are the essential characteristics for the present discussion.

[5] Λ is the quantum number of electronic orbital angular momentum around a line joining the nuclei—commonly called i_l or σ_k.

[6] To be complete, another factor [ψ (co-ördinates of centre of gravity of molecule)] should be added, but this is unaffected by an interchange $1 \rightleftharpoons 2$ or $a \rightleftharpoons b$ and so need not be included here. The co-ördinates x, y, z here are *relative* to the centre of gravity.

[7] The interchange $1 \rightleftharpoons 2$ does not affect the second or fourth factor (one may say, if one wishes, that these factors are always SyE); the interchange $a \rightleftharpoons b$ does not affect the third factor (always SyP).

[8] *Cf.* F. Hund, *Z. Physik*, **51**, 762 (1928).

[9] *Cf.* W. Weizel, *Z. Physik*, **54**, 321 (1929) for an excellent summary.

[10] *Cf.* P. M. Morse and E. C. G. Stueckelberg (*Physical Rev.*, **33**, 932, 1929) for a treatment of the H_2^+ problem.

[11] The above expression for $\psi_{el}(x_1 \ldots z_b)$—let us call it $\psi(12)$.—is neither SyE nor AnE, and is not really adequate (*cf.* discussion below of the factor $\psi(s_1 s_2)$). The derived expressions $\psi(12) + \psi(21)$ and $\psi(12) - \psi(21)$ are, however, respectively SyE and AnE, and it is these latter,—corrected for interactions of the electrons,—which must be used in the correct final ψ. If the SyE form is used, the factor $\psi_{el}(s_1 s_2)$ in equation (1) must be AnE, and *vice versa*, in order that the complete ψ expression shall be AnE, as required. All this, however, has no effect on the symmetry properties of ψ in the *protons*, which mainly interest us here; hence it is sufficient for the latter to consider $\psi(12)$.

go over on union of the nuclei into the ordinary n and l of the united atom.[9, 10]. It is convenient to designate $l = 0, 1, 2 \ldots$ by letters s, p, $d \ldots$ as in atoms, also $\lambda = 0, 1, 2 \ldots$ by letters $\sigma, \pi, \delta \ldots$; thus an electron having $n = 3$, $l = 2$, $\lambda = 1$ ($n_\xi = 0$, $n_\eta = 1$, $| n_\phi | = 1$) would be called a $3d\pi$ electron. In addition to these individual quantum numbers, we need a resultant quantum number $\Lambda = | n_{\phi 1} + n_{\phi 2} |$; also s for individual and S for resultant spin (s_1, s_2, S_e for the electrons, s_a, s_b, S_p for the protons). There is also a rotational quantum number K, often also a J (J = resultant of K and S_e).[12]

If in the ψ_{el} function[11] given by equation 2 we interchange indices $a \rightleftharpoons b$, we have $\xi \to \xi$, $\eta \to -\eta$, and the positive direction of ϕ becomes the negative, while $\psi(\xi) \to \psi(\xi)$, $\psi(\eta) \to +\psi(\eta)$ or $-\psi(\eta)$, and $\psi(\phi) \to +\psi(\phi)$ or $-\psi(\phi)$; *i.e.*, $\psi(\xi)$ is SyP, $\psi(\eta)$ is SyP or AnP, $\psi(\phi)$ is SyP or AnP. As is easily shown, [8, 9] $\psi(\eta)$ is SyP if $l - \lambda$ is even, AnP if $l - \lambda$ is odd, while $\psi(\phi)$ is SyP if $\lambda = 0$, but is double with one component SyP, one AnP, if $\lambda > 0$. The complete ψ_{el} is SyP or AnP according as the number of AnP factors, including those for both electrons, is even or odd. For $\Lambda = 0$, ψ_{el} is *either* SyP or AnP; for $\Lambda > 0$, it is always *double* with one component SyP, one AnP.

Although the quantum numbers n, l, λ lose their sharpness of meaning, and ψ_{el} ceases to be factorable, in the actual case in which the electrons exert Coulomb forces on each other, the symmetry properties above described, and their relations to l, λ, and Λ remain.[11]

Turning now to the second factor in equation 1, let us consider first the case $\Lambda = 0$ (Σ states). Here $\psi_{\ nuclear}(x_a \ldots z_b) = \psi(R)\psi(\Theta, \Phi)$, Θ being the angle between the axis $a \to b$ and an arbitrary axis fixed in space, and Φ being the azimuth of the axis $a \to b$ with reference to the fixed axis. $\psi(\Theta, \Phi)$ is an ordinary spherical surface function, the total number of nodes in Θ and Φ being given by the quantum number K; $\psi(R)$ corresponds to the vibrations of the nuclei. In the interchange $a \rightleftharpoons b$, we have $R \to R$, $\Theta \to \pi - \Theta$, and $\Phi \to \pi + \Phi$; $\psi(R) \to \psi(R)$ always (SyP), $\psi(\Theta, \Phi) \to +\psi(\Theta, \Phi)$ if K is even (SyP) and $-\psi(\Theta, \Phi)$ if K is odd (AnP). Similar relations hold if $\Lambda > 0$.

The third factor in equation 1 is capable of being either SyE or AnE, according as the first factor is AnE or SyE.[11] The behaviour of the electron spins can best be understood by first assuming them to be placed in an external magnetic field. Each spin has just two possible orientations with reference to the field, parallel (+) or anti-parallel (−). If we assume no interaction between the two spins, we have the following possibilities for $\psi_{el}(s_1 s_2)$:

$$\psi_{el}(s_1 s_2) = \psi_1{}^+\psi_2{}^+, \text{ or } \psi_1{}^+\psi_2{}^-, \text{ or } \psi_2{}^+\psi_1{}^-, \text{ or } \psi_1{}^-\psi_2{}^-.$$

The first and fourth possibilities are both SyE; but the second and third —which, moreover, have the same energy, different, however, from both

[12] If $S_e = 0$ (singlet states, as in par-H_2, par-He_2, etc.) $J \equiv K$. If $S_e > 0$, J has values $K + S_e, K + S_e - 1, \ldots K - S_e$, if there is an appreciable interaction energy between K and S_e; otherwise J is undefined. In many of the H_2 and He_2 states having $S_e = 1$ (ortho-H_2 and ortho-He_2) the interaction energy of K and S_e is extremely small because of the small nuclear charges, so that J, even when it exists, is of minor importance. In such cases, J (ordinarily written j) is now commonly used where K *ought* to be used; this practice arose because of the fact that the possibility of an $S_e > 0$ was at first dismissed or overlooked. Although J would still be permissible for *singlet* states, it seems best, in H_2 and He_2, always to use K for the essential rotational quantum number, whether $S_e = 0$ or 1, especially since one does not always know S_e. For molecules containing heavier atoms, K is still always the important quantum number if $\Lambda = 0$; if $\Lambda > 0$, K is important in Hund's case b (weak coupling of S_e) but loses its meaning in Hund's case a (strong coupling of S_e), where J is important.

the other two—are neither *SyE* nor *AnE*. When allowance is made for a slight interaction of the two spins, it turns out that, as a result of the well-known quantum-mechanical resonance effect, $\psi_1^+\psi_2^-$ and $\psi_2^+\psi_1^-$ are replaced by $\psi_1^+\psi_2^- + \psi_2^+\psi_1^- + V_{12}^{Sy}$ and $\psi_1^+\psi_2^- - \psi_2^+\psi_1^- + V_{12}^{An}$, the former being *SyE*, the latter *AnE* (V_{12}^{Sy} and V_{12}^{An} are small interaction terms). Thus, two electron spins in a magnetic field give three *SyE* terms and one *AnE* term. The three former represent the three magnetic states associated with a resultant spin $S_e = 1$ (triplet or ortho-H_2 electron states), while the last belongs to $S_e = 0$ (singlet or par-H_2 electron states).

The fourth factor in equation 1 must, according to the antisymmetry requirement, be *SyP* if the product of the first and second factors is *AnP*, and *vice versa*. (The third factor does not affect the result, since it depends only on the electrons; in other words, it acts *SyP*.) If protons, like electrons, have a spin quantum number $s = 1/2$, then two protons spins must give two possible resultants, $S_p = 1$(*SyP* type) and $S_p = 0$(*AnP* type). The behaviour of proton spins and their functions in a magnetic field should be exactly analogous to that of electron spins (*cf.* preceding paragraph). On account of their three magnetic sublevels, states with $S_p = 1$ should have, other things being equal, three times the statistical weight of those with $S_p = 0$.

Specific Heat and Band Spectra.—The normal electron state of H_2 is undoubtedly a $1s\sigma^2\ ^1\Sigma$ state (two $1s\sigma$ electrons, and $\Lambda = 0$, $S_e = 0$) derived from two normal H atoms (each $1s\ ^2S$). Since l_1, l_2, λ_1, λ_2 are all zero, this state is evidently *SyP* so far as the first factor in equation 1 is concerned. [It is also, incidentally, *SyE* in the first factor, and *AnE* in the third factor.] Since $\Lambda = 0$, this state of H_2 would then be *SyP* for $K = 0, 2, 4, \ldots$, *AnP* for $K = 1, 3, 5 \ldots$ as a result of the first and second factors. Now, in order that the *complete* ψ shall always be *AnP*, the fourth factor must be *AnP* for $K = 0, 2, 4 \ldots$, *SyP* for $K = 1, 3, 5 \ldots$ Hence the rotational levels of normal H_2 should be divided into two classes, namely, levels with even K values, $S_p = 0$, and a weight $2K + 1$, and levels with odd K values, $S_p = 1$, and weight $3(2K + 1)$.[13] For statistical equilibrium, the populations of the various rotational levels should be proportional to these statistical weights multiplied by the Boltzmann factor:

$$e^{-Energy/kT} \left(= e^{-BK(K+1)/kT} \text{ here} \right).$$

We have now to consider an important fact: transitions involving the change $S_p = 1 \rightleftharpoons Sp = 0$ may be expected to occur only at an exceedingly slow rate,[14] even under the influence of collisions. This is essentially because of the very slight coupling between the proton spins and other elements (nuclear rotation, electron motion and spins) of the molecule.[2, 3]

The preceding considerations are of importance when one considers the behaviour of a sample of hydrogen gas, initially in thermal equilibrium, when the temperature is changed. Calculation shows that in the gas at room temperature, the molecules should be distributed over

[13] Each rotational level of a Σ state should split into $(2K + 1)(2S_e + 1)(2S_p + 1)$ levels in a magnetic field. Here, $S_e = 0$.

[14] Radiative transitions $\Delta K = \pm 1$ do not occur with appreciable intensity in homopolar molecules unless the electron state also changes. Transitions $\Delta K = \pm 2$ are found in the Raman effect in H_2 (J. C. McLennan and J. H. McLeod, *Nature*, 2nd Feb., 1929), but these involve no change in S_p.

several odd and even K values in such a way that the sum total of molecules having $S_p = 1$ is nearly three times that having $S_p = 0$. If, now, the temperature is lowered, the equilibrium distribution tends toward lower K values, involving incidentally a shift toward an increasing fraction of molecules with $S_p = 0$; for thermal equilibrium at 0° absolute all molecules would be in the level $K = 0$, which has $S_p = 0$. But, on account of the slowness of the change $S_p = 1 \rightleftharpoons S_p = 0$, true equilibrium is not to be expected in ordinary experiments, but only a sort of partial equilibrium in which the molecules with each value of S_p independently distribute themselves according to $(2K + 1)e^{-BK(K+1)/kT}$. Near $T = 0$, after cooling in the ordinary manner from room temperature, about three-quarters of the molecules would be expected to accumulate in state $K = 1$, one-quarter in state $K = 0$. Dennison has shown [3] that the ordinary observed specific heat data on hydrogen gas at low temperatures can be correctly reproduced by calculation if this behaviour is assumed.

On the other hand, Bonhoeffer and Harteck, and Eucken,[15] have recently shown that the transformation of $S_p = 1$ ("ortho–H_2" of Bonhoeffer and Harteck) [16] into $S_p = 0$ ("para–H_2" of Bonhoeffer and Harteck),[16] from the room temperature equilibrium ratio of 3 : 1 toward the zero degree equilibrium ratio of 0 : 1, actually proceeds, very slowly as expected, in cold hydrogen gas kept under very high pressures so as to increase the frequency of collisions, or kept in the presence of charcoal. The changing ratio is followed by means of the changing specific heat of the gas, which behaves like a mixture of two gases with different specific heat curves. An interesting result of this work is that, just as in cooling ordinary hydrogen below room temperature the 3 : 1 ratio in favour of $S_p = 1$ is ordinarily preserved, so in warming hydrogen which has been kept near 0° in charcoal, the 0 : 1 ratio characteristic of the latter temperature is preserved (*cf.* below).

The above results confirm the theory that there are two almost non-combining systems of rotational levels in normal H_2 and further show that it is the even levels which have the lower statistical weight, all this being in accordance with the assumption that ψ must always be AnP, and that this is made possible for all K values by means of a proton spin.

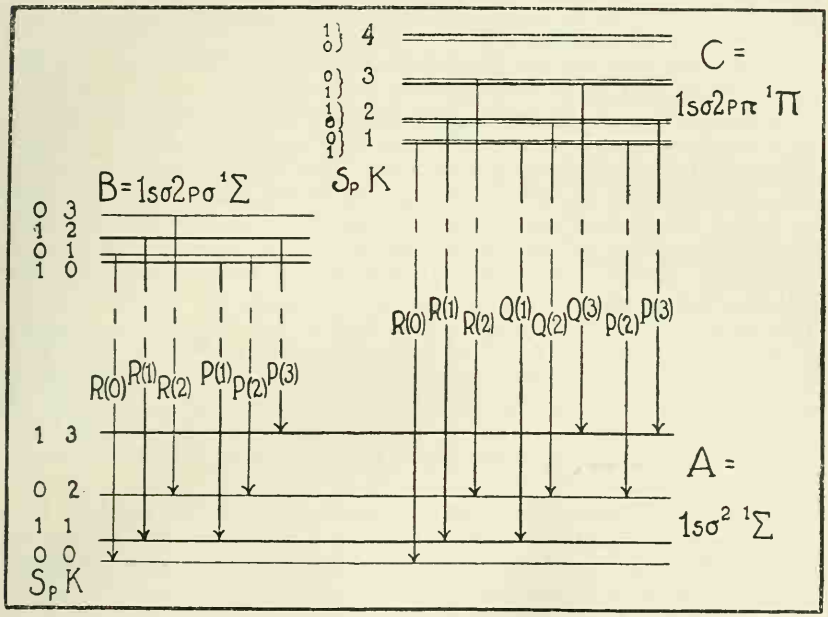
Spectroscopically, the 3 : 1 statistical weight ratio in favour of the $S_p = 1$ states shows itself in the occurrence of alternating intensities in the hydrogen bands when ordinary hydrogen is used. Perhaps the two most important H_2 band systems are the far ultra-violet absorption and emission systems $A \rightleftharpoons B$ (Lyman bands) and $A \rightleftharpoons C$ (Werner bands). State A is the normal state $1s\sigma^2\,{}^1\Sigma$, B is a $1s\sigma 2p\sigma\,{}^1\Sigma$ state, C is a $1s\sigma 2p\pi\,{}^1\Pi$ state. In these bands, each branch shows alternating intensities,[17] the stronger lines being those connecting the levels $K = 1, 3, 5 \ldots$ of state A with levels $K = 0, 2, 4 \ldots$ of state B (P and R branches); or with levels $K = 1, 3, 5 \ldots$ of the state C (Q branches) or 2, 4, 6 . . . of state C (P and R branches). The figure shows these relations graphi-

[15] K. F. Bonhoeffer and P. Harteck, *Naturwiss.*, **17**, 182, 321 (1929); *Preuss. Akad. der Wiss., Physik, Math. Klasse*, 1929, VII.; *Z. physik. Chem.*, **4A**, 113 (1929); A. Eucken, *Naturwiss.*, **17**, 182 (1929).

[16] The use of the designation ortho–H_2 for the $S_p = 1$ rotational levels and para–H_2 for the $S_p = 0$ levels seems inadvisable, because these terms are already in use to distinguish the systems of electron levels with $S_e = 1$ and $S_e = 0$ respectively.

[17] *Cf.* T. Hori, *Z. Physik*, **44**, 834 (1927); H. H. Hyman and R. T. Birge, *Nature*, **123**, 278 (1929), etc.

cally and also shows how the stronger lines are all associated with $S_p = 1$, the weaker ones with $S_p = 0$. For state B, the factor $\psi_{el}(x_1 \ldots z_b)$ of equation 1 is AnP, since $(l_1 - \lambda_1) + (l_2 - \lambda_2)$ is odd; hence for $K = 0$, 2 . . ., $\psi_{nuclear}(\Lambda, x_a \ldots z_b)$ being SyP, $\psi_{nuclear}(s_a s_b)$ has to be SyP, which requires $S_p = 1$, instead of $S_p = 0$ as for the even levels of state A. Or reasoning in the reverse direction, we may say that since $K = 0$, 2 . . . are strong (hence $S_p = 1$) for state B, $\psi_{el}(x_1 \ldots z_b)$ must be AnP, hence $(l_1 - \lambda_1) + (l_2 - \lambda_2)$ must be odd. Since we know B is a $^1\Sigma$ state (bands with only P and R branches are necessarily $\Sigma \rightleftharpoons \Sigma$), this practically requires $1s\sigma np\sigma$ as the electron configuration, since *two* electrons are surely not excited; furthermore, $n = 2$ is quite sure, since B is the lowest excited $^1\Sigma$ state. Proceeding in a similar way, the assignment $1s\sigma 2p\pi\ ^1\Pi$ is practically certain for state B. (The existence of P,



Q, and R branches in $C \rightleftharpoons A$ and of two rotational levels for each value of K require a Π state.)

Of the visible H_2 bands, the series of systems paralleling the atomic lines H_α, H_β, H_γ . . . are among the best known. These systems have the same type of structure and alternating intensities as the Werner bands, and as Richardson and Das have concluded,[17a], represent transitions $n^3\Pi \rightarrow 2^3\Sigma$ (or perhaps $n^1\Pi \rightarrow 2^1\Sigma$). From the position of the $^3\Sigma$ level and the intensity relations (odd K levels stronger in $^3\Sigma$), it is evident that this state is $1s\sigma 2s\sigma$, while the $^3\Pi$ states are doubtless $1s\sigma np\pi$, with $n = 3$ for the H_α bands.

Bonhoeffer and Harteck[18] have recently reported an interesting spectroscopic experiment, using hydrogen which has been in equilibrium at a very low temperature so that practically all the molecules have

[17a] O. W. Richardson and K. Das, *Proc. Roy. Soc.*, **122A.**, 688 (1929); intensity relations, Kapuscinski and Eymers, *Proc. Roy. Soc.*, **122A.**, 58 (1929).

[18] Bonhoeffer and Harteck, *Z. physik. Chem.*, **4B**, 138 (1929).

$S_p = 0$. On warming to room temperature, the molecules distribute themselves over the levels $K = 0, 2, 4 \ldots$, and in the H_α bands ($3^3\Pi \rightarrow 2^3\Sigma$) of the secondary spectrum every other line is now practically *missing* in each branch, instead of merely weak; further, the missing lines are just those which in ordinary hydrogen are the stronger.

Molecules with Complex Nuclei.

Theoretical Considerations.—In other homopolar molecules than hydrogen, each nucleus contains P protons and E electrons; in addition, there are $N = P - E$ external electrons per atom (N = nuclear charge). The fact that the nuclei are no longer simple protons necessitates some amplification of the theory. In place of equation 1 we may now write

$$\psi = [\psi_{el}(x_1 \ldots z_{2N} X_a \ldots Z_b)][\psi_{\ nuclear}(\Lambda,\ X_a \ldots Z_b)][\psi_{el}(s_1 \ldots s_{2N})]$$
$$[\psi_{\ nuclear}(x,\ y,\ z,\ s \text{ co-ördinates of nuclear electrons and protons})] \quad (3)$$

The external electrons are designated here by indices $1 \ldots 2N$, the centers of gravity of the two nuclei by a and b.

Suppose in ψ of equation 3 we interchange any two protons (or electrons) one of which is in each nucleus. According to the antisymmetry rule, ψ must be of such a form that it is changed to $-\psi$ by this operation. If we now interchange a second pair, $-\psi \rightarrow \psi$; and so on. If we continue until all nuclear particles have been interchanged, $\psi \rightarrow \psi$ is evidently required for the net result if N is even, but $\psi \rightarrow -\psi$ if N is odd, since $P + E = N + 2E$ is even if N is even, and *vice versa*. But this net result is precisely the same as would be obtained by an interchange of the two complete nuclei ($a \rightleftharpoons b$). Hence, $a \rightleftharpoons b$ must cause $\psi \rightarrow \psi$ or $\psi \rightarrow -\psi$: ψ must be symmetrical in the nuclei (SyN) for N even, but antisymmetrical (AnN) for N odd. Any real state of a molecule must now meet the following requirements: (*a*) the product of the first, third, and fourth factors of equation 3 must be AnE; (*b*) the product of the first, second and fourth factors must be SyN if N is even, AnN if N is odd.

All that was said about symmetry in the *protons* for the first and second factors of equation 1 is equally applicable here with respect to symmetry in the *nuclei* for the first and second factors of equation 3. The *fourth* factor of equation 3 is, however, somewhat different from that of equation 1. If an atomic nucleus is assumed to be capable of a number of quantum states, each of these, and in particular, the normal state, presumably has a quantum number j_n representing the total angular momentum, analogous to the quantum number j of the outer electrons of the atom.[19] (This j_n may be a resultant of proton spins, electron spins, and perhaps other elements of angular momentum.) When two identical nuclei, each in its normal state, are present in a molecule, we may suppose a very weak coupling of the two j_n's, similar to that of the proton spins in H_2, giving several resultants $J_n = 2j_n$, $2j_n - 1, \ldots, 0$. The resultants $2j_n$, $2j_n - 2, \ldots$ should be SyN while $2j_n - 1$, $2j_n - 3 \ldots$ should be AnN. This can be seen by first assuming each j_n separately oriented in an external magnetic field (magnetic quantum numbers m_a and m_b). For this system we have a number of possible states such as $m_a = j_n$, $m_b = j_n$, $j_n - 1 \ldots, -j_n$; $m_a = j_n - 1$, $m_b = j_n$, $j_n - 1, \ldots - j_n$; and so on. The states ($m_a = j_n = m_b$) and ($m_a = -j_n = m_b$) each occur just once, and the

[19] I am indebted to Professor W. Heisenberg for this suggestion.

corresponding fourth ψ factors of equation 3 ($\psi_a^j\psi_b^j + V_{Sy}^{jj}$ and $\psi_a^{-j}\psi_b^{-j} + V_{Sy}^{-j,-j}$) are SyN (the V's are small SyN functions corresponding to the coupling of the nuclei). Similarly with states ($m_a = j_n - 1 = m_b$) and ($m_a = -[j_n - 1] = m_b$), and so on until we reach $m_a = m_b = 0$ or $\pm 1/2$. All other states occur in pairs of equal energy,[19a] such as $m_a = j_n$, $m_b = j_n - 1$ and $m_a = j_n - 1$, $m_b = j_n$, corresponding, when the coupling of the nuclei is neglected, to $\psi_a^j\psi_b^{j-1}$ and $\psi_b^j\psi_a^{j-1}$; from each degenerate pair of ψ functions of this kind we obtain, as a result of the quantum-mechanical resonance effects,[19a] two new functions, one SyN (as $\psi_a^j\psi_b^{j-1} + \psi_b^j\psi_a^{j-1} + V_{Sy}^{j,j-1}$) and one AnN (as $\psi_a^j\psi_b^{j-1} - \psi_b^j\psi_a^{j-1} + V_{An}^{j,j-1}$). The set of ψ functions obtained in the above way can now be divided into groups corresponding to the various values of J_n. Thus, to go with $J_n = 2j_n$ we use $2J_n + 1$ SyN functions, including necessarily ($\psi_a^j\psi_b^j + V_{Sy}^{jj}$) and ($\psi_a^{-j}\psi_b^{-j} + V_{Sy}^{-j-j}$); then for $J_n = 2j_n - 1$ we have $2J_n + 1$ AnN functions; and so on, with finally a single function (SyN or AnN, according as j_n is an integer or half integer) corresponding to $J_n = 0$. For each J_n the statistical weight is $2J_n + 1$. The following table shows for various values of j_n the relative weights and symmetry properties for the possible J_n values. The table also gives for each j_n value, the ratio of the *sum* of the weights of all the SyN values of J_n to the sum of the weights of all AnN values. This ratio, as we shall see, is that which should govern the alternating intensities of band lines.

TABLE I.

j_n.	J_n.	Weight.	Symmetry.	Ratio of Weights. $SyN : AnN$.
0	0	1	SyN	1 : 0
1/2	1	3	SyN	3 : 1
	0	1	AnN	
1	2	5	SyN	
	1	3	AnN	2 : 1
	0	1	SyN	
3/2	3	7	SyN	
	2	5	AnN	5 : 3
	1	3	SyN	
	0	1	AnN	
2				3 : 2
∞				1 : 1

Considering first the case $\Lambda = 0$, we note that the first factor in equation 3 may be either SyN or AnN, according to whether Σl_τ ($= l_1 + l_2 + \ldots + l_{2N}$) for the electrons is even or odd; the second factor is SyN for K = even, AnN for K = odd; while the fourth factor is capable (unless $j_n = 0$) of making the *resultant state* either SyN or AnN, the former being required if N is even, the latter if N is odd. The rotational levels for any one electronic state should, therefore, have alternately values of J_n which correspond to a SyN and to an AnN factor.

[19a] If the coupling between the nuclei were really zero, there would usually be more than two states with equal energy; *e.g.* $(j_n - 1, j_n - 1)$, $(j_n, j_n - 2)$, $(j_n - 2, j_n)$. But when this coupling is considered (without considering yet the quantum-mechanical resonance), only such pairs as $(j_n, j_n - 2)$ and $(j_n - 2, j_n)$ remain equal in energy.

For example, if N is even, Σl_τ is odd, and $j_n = 1$, the rotational levels $K = 0, 2, 4, \ldots$ have $J_n = 1$, while for each of the values $K = 1, 3, 5 \ldots$, one-sixth of the molecules have $J_n = 0$, five-sixths, $J_n = 2$. Taken as a whole, the odd K levels have twice the statistical weight of the even K levels (*cf.* Table I.).

When $\Lambda > 1$, each rotational level is double; the first factor in equation 3 is SyN for one sub-level, AnN for the other; the second factor is either SyN or AnN, depending on the value of K; while the nuclear spin factor (unless $J_n = 0$) is capable of making the resultant state either SyN or AnN. Thus, in each double rotational level, one component has a value, or has values, of J_n corresponding to a SyN spin factor, the other has a value or values corresponding to an AnN factor; as a result, the upper and lower components alternately have the greater weight.

In the frequent case where $j_n = 0$ we have only $_n = 0$, which corresponds only to a SyN factor, so that if $\Lambda = 0$ and Σl_τ is even, only the rotational states $K = 0, 2, 4 \ldots$ are possible, while if $\Lambda = 0$, and Σl_τ is odd, only $K = 1, 3, 5 \ldots$ are possible (assuming N even in both cases). If $j_n = 0$ and $\Lambda > 0$, alternately the upper and the lower component of each rotational level is missing.

Table II. is a summary of some of the expected relations for homopolar molecules, arranged for convenience of comparison with experimental data. It is assumed that, as would be expected, j_n is integral or half integral, according as $P + E$, hence N ($N = P - E$), is even or odd.

TABLE II.

N.	Allowed ψ Type.	j_n.	J_n.	Symm. of fourth factor of Eq. 3.	Rel. Weight.	Allowed K values for $\Lambda = 0$.	
						Σl_τ even.	Σl_τ odd.
even	SyN	0	0	SyN	1	even	odd.
odd	AnN	1/2	1	SyN	3	odd	even.
			0	AnN	1	even	odd.
even	SyN	1	2, 0	SyN	2	even	odd.
			1	AnN	1	odd	even.
odd	AnN	3/2	3, 1	SyN	5	odd	even.
			2, 0	AnN	3	even	odd.
even	SyN	2	4, 2, 0	SyN	3	even	odd.
			3, 1	AnN	2	odd	even.
odd	AnN	5/2	5, 3, 1	SyN	7	odd	even.
			4, 2, 0	AnN	5	even	odd.

Applications of Theory, and Difficulties.—Table III. summarises the experimental information now existing on alternating intensities in band spectra, and gives conclusions, where possible, as to j_n and Σl_τ values. Data on *band line* intensities are in most cases not given directly in the table, but have been interpreted in terms of relative weights of *rotational levels*. The observed band line intensities in every case are, however, in harmony with the interpretation given.

TABLE III.

Molecule.	References.	Electron Transitions.	Strong Levels.	Conclusions.		Nuclear Particles	
				Σ^{+}_{-}	j_n	P	E
H_2	3, 14, 15, 17, 17*a*, 18, 21	$A^1\Sigma \rightarrow A^1\Sigma$ (Raman effect	$A^1\Sigma$, and $2^3\Sigma$, odd K (3 : 1)	even			
		$B^1\Sigma \rightarrow A^1\Sigma$	$B^1\Sigma$, even K (3 : 1)	odd	1/2	1	0
		$C^1\Pi \rightarrow A^1\Sigma$	$C^1\Pi$, and $n^3\Pi$, { odd K in Q (3 : 1)				
		$n^3\Pi \rightarrow 2^3\Sigma$ (H_α, H_β, H_γ, . . . bands)	{ even K in P, R (3 : 1)				
He_2	9	Triplet, singlet $\Pi \rightarrow \Sigma$ $\Sigma \rightarrow \Pi$ $\Delta \rightarrow \Pi$	Only odd K levels in observed Σ states; only odd K in Q branch, only even K in P, R branches, for Π levels	odd for Σ states	0	4	2
C_2	20	$^3\Pi \rightarrow {}^3\Pi$ (Swan bands)	Rotational levels double, upper and lower alternately missing		0	12	6
N_2	21	$X^1\Sigma \rightarrow X^1\Sigma$ (Raman effect)	$X^1\Sigma$, even K	odd	>0		
	20	$^3\Pi \rightarrow {}^3\Pi$ (2nd pos. N_2 bands)	Rotational levels double, upper and lower alternately weaker			14	7
N_2^+	22, 23	$A'^2\Sigma \rightarrow X'^2\Sigma$	$X'^2\Sigma$, even K (2·0 : 1)	odd	1? or mixture	14	7
			$A'^2\Sigma$, odd K (2·0 : 1)	even			
$(O_{16})_2$	24	$A^1\Sigma \leftarrow X^3\Sigma$ $B^3\Sigma \leftarrow X^3\Sigma$	$X^3\Sigma$, odd K only; $A^1\Sigma$ and $B^3\Sigma$, even K only	odd even	0	16	8
F_2	25	$^1\Sigma \rightarrow {}^1\Pi$	$^1\Pi$ { even K in Q branch ($\backsim$ 3 : 1) odd K in P, R branches ($\backsim$ 3 : 1)		1/2	19	10
			$^1\Sigma$, even K ($\backsim$ 3 : 1)	odd			
Na_2	26	$^1\Pi \leftarrow {}^1\Sigma$	No alternation detected		5/2 or more	23	12
$(Cl_{35})_2$	27	$^1\Sigma \leftarrow {}^1\Sigma$	Lower $^1\Sigma$, odd K ($\backsim$ 1·4 : 1)	even	5/2 ?	35	18
			Upper $^1\Sigma$, even K ($\backsim$ 1·4 : 1)	odd			
I_2		$^1\Sigma \rightleftharpoons {}^1\Sigma$	No alternation detected		5/2 or more	127	74
Bi atom	1				9/2	209	126

[20] *Cf.* R. S. Mulliken, *Physical Rev.*, **29**, 637 (1927) for summary.
[21] F. Rasetti, *Nature*, **123**, 757 (1929); *Proc. Nat. Acad. Soc.*, **15**, 515 (1929); *Physical Rev.*, **34**, 367 (1929).
[22] R. de L. Kronig, *Naturwiss.*, **16**, 335 (1928).
[23] L. S. Ornstein and W. R. van Wyck, *Z. Physik*, **49**, 315 (1928).
[24] R. S. Mulliken, *Physical Rev.*, **32**, 880 (1928).
[25] H. G. Gale and G. S. Monk, *Astrophys. J.*, **49**, 77 (1929).
[26] Na_2 Bands, F. W. Loomis and R. W. Wood, *Physical Rev.*, **32**, 236 (1928).
[27] A. Elliott, *Proc. Roy. Soc.*, **123A.**, 629 (1929)

The j_n values in Table III. present some interesting problems. The value $j_n = 1/2$ for H is interpreted as a proton spin. The value $j_n = 0$ in the atoms He, C, and O_{16}, all of whose nuclei are multiples of a group of 4 protons and 2 electrons, suggests a nuclear configuration analogous to a ^1S atomic state, with proton and electron spins perhaps all cancelling in pairs. The probable value $j_n = 1/2$ for F is not surprising, since an odd number of spins should be present if each particle has one. The relatively large values of j_n, for Na, Cl_{35}, I, and Bi suggest that,—as often also in the normal state of (the planetary electron configuration of) an atom,—the normal state of a nucleus does not necessarily correspond to a maximum pairwise cancellation of spins.

The value $j_n = 1$ which is definitely indicated for N by the measured [23] alternating intensity ratio 2·0 : 1 in N_2^+ is very puzzling, since it cannot be accounted for ($P + E$ being odd) by electron and proton spins setting themselves parallel or antiparallel. Of course, there may also be nuclear angular momentum of another type (roughly corresponding to orbital angular momentum of outer electrons), but even this cannot account for $j_n = 1$ unless it contributes an odd number of half-integer units to j_n, contrary to our experience with the outer electrons of atoms. We are left with the possibility, suggested by Kronig,[22] that ordinary nitrogen happens to be a mixture of two or more isobaric isotopes of different j_n in just such a proportion as to account for the 2·0 : 1 intensity ratio. Such isobaric isotopes would presumably be somewhat analogous to isomers of a complex molecule, as, for example, hexane.

Some interesting data on alternating intensities are found in the Raman effect in H_2, N_2, and O_2. The scattered light here contains frequencies corresponding to changes $\Delta K = \pm 2$ (these obviously are possible without change in J_n). In ordinary liquid H_2 (in which rotations can apparently take place about as freely as in H_2 gas) McLennan and McLeod [14] find the two transitions $0 \rightarrow 2$ and (stronger) $1 \rightarrow 3$; the relative intensities observed here are explained on the same basis as the specific heat of H_2 gas (*cf.* above) and give further confirmation of the conclusion that $S_p = 1 \rightarrow S_p = 0$ proceeds extremely slowly in H_2. In gaseous H_2 Rasetti [21] finds alternating intensities of the expected type (odd K values stronger). In O_2 gas, Rasetti finds transitions between odd K levels only, such as $9 \rightarrow 11$, $11 \rightarrow 13$, in agreement with the band spectrum evidence. In N_2 he finds that transitions between even K levels (such as $6 \rightarrow 4$, $6 \rightarrow 8$, $8 \rightarrow 10$, . . .) are stronger than those between odd K levels (as $7 \rightarrow 9$, etc.); band spectrum data are lacking here. This result presents a serious difficulty, which exists independently of the difficulty already discussed in regard to the value of j_n for the N nucleus. Whatever the value (or values) of j_n, the K levels which are stronger (here the even ones) should be SyN levels with respect to the fourth factor of equation 3. But, since the nuclear rotational factor, corresponding to K, is here also SyN ($\Lambda = 0$, $K =$ even), the ψ_{el} factor (first factor in equation 3) must be AnN, and it follows that Σl_τ must be odd. This, however, is contradictory to Hund's and the writer's well-founded conclusions [28] that normal N_2 has an electron configuration ($1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^4 3s\sigma^2$) composed of closed shells. The contradiction is evident from the fact that every closed shell always contains an even number (two or four) of equivalent electrons (equivalent electrons are alike in n, l, and λ). It would seem either that there

[28] R. S. Mulliken, *Physical Rev.*, **32**, 204 (1928); F. Hund, *Z Physik*, **51**, 759 1928).

is an error in Rasetti's measurements or that the requirement that ψ shall be AnP and $An\Sigma$ in equation 3 is incorrect for molecules with complex nuclei, or that something has been overlooked in its application here. The latter possibilities receive support from the fact that the observed K values (odd values) in $(O_{16})_2$ lead, according to Table II., to $\Sigma l_\tau =$ odd, contrary to the writer's interpretation [28] of the electron configuration of normal O_2; of course, the latter may be wrong, but it seems unlikely that O_2 can have a configuration as different from that suggested as would be necessary to give $\Sigma l_\tau =$ odd.

Although in I_2 no alternation of intensities has been detected in the band lines, the expected existence of molecules differing in J_n and in the symmetry of the fourth factor of equation 3 is shown by some work of Wood and Loomis.[29] They find that when I_2 is excited, by means of monochromatic light, to a single rotational level (*e.g.*, $K = 34$ of the 26th vibrational level of the upper $^1\Sigma$ electron level of the visible I_2 absorption bands), and then, before radiating, suffers collisions with He atoms, the collisions cause changes only of an even number of units in K, to $K = 30, 32, 36, 38$, etc. This can be explained somewhat as follows. Suppose $j_n = 5/2$ for the I atom and suppose Σl_τ is odd for the upper $^1\Sigma$ level; then for $K = 34$ and other even levels (*cf.* Table II.) we have the molecules distributed over the values $J_n = 1, 3$, and 5, while for the odd levels, $J_n = 0, 2, 4$. Since changes in J_n in collisions are very improbable, we expect $J_n = 1 \rightarrow J_n = 1$, $J_n = 3 \rightarrow J_n = 3$, $J_n = 5 \rightarrow J_n = 5$ in collisions, which requires $K =$ even $\rightarrow K =$ even in all cases.

Molecules with Unequal Nuclei.

In agreement with the theory, alternating intensities have not been found in molecules with unequal nuclei. This fact is particularly striking in the case of molecules containing isotopic atoms. Thus, in $(O_{16})_2$, every other rotational level (K value) and band line is missing, but in $O_{16}O_{17}$ and $O_{16}O_{18}$, all values of K are present, and there are no missing band lines, nor even alternating intensities.[30] Again, in the case of Cl_2, the $(Cl_{35})_2$ bands show alternating intensities,[27] while corresponding $Cl_{35}Cl_{37}$ bands show no alternations.

If isobaric isotopes are capable of stable existence, as seems to be indicated in the case of N_{14}, even these should fail to show alternating intensities if two such isotopes are combined in one molecule.

[29] I_2 Bands, effect of collisions; F. W. Loomis and R. W. Wood, *J. Franklin Inst.*, **205**, 491 (1928).

[30] W. F. Giauque and H. L. Johnston, *J. Am. Chem. Soc.*, **51**, 1436 (1929); *Nature*, Mar. 2 and June 1, 1929; H. D. Babcock, *Nature*, **123**, 761 (1929) and *Proc. Nat. Acad. Sci.* (1929).

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CHEMICAL BINDING.

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Two or more atoms or ions can form a molecule, if the energy of the complete molecule is less than the sum of the energies of the separate atoms or ions. Whether that is the case can be decided by a very complicated and laborious calculation, using the new quantum mechanics. We cannot satisfactorily use such a calculation; in order to understand chemical binding, we look for simple properties of the atoms which lead us to expect a positive or a negative result from the calculation. It may be that there are different conditions, enabling atoms to form compounds, which can work against each other. It is in that case not possible, in a single case, to predict whether there is binding or not; nevertheless we can say that we understand binding.

In addition to some very general considerations (Mulliken, Hund), the only definite results upon chemical binding are given by Heitler and London.[1] London shows a parallelism between the conception of chemical valency which has arisen empirically, and some properties of atoms in quantum mechanics. He does not make it plausible that from the energetic point of view, those atomic properties are favourable for binding. In the following note, therefore, we shall seek generally to ascertain the properties which enable atoms to form bindings, and shall consider which of them lead, under certain conditions, to London's conception. It may be expected, that binding will appear as a very complex phenomenon.

Let us consider two pairs of atoms H + H and He + H in their fundamental states. The one can form a molecule (H_2), the other probably not (HeH). To get a qualitative picture of the terms of a molecule, we consider the corresponding system of two fixed centres at different distances between the centres. Neglecting at first the energy coming from the repulsive force between the two centres, we have a system which at large distances passes over into two atoms (or ions) and at small distances into one atom. Its terms can be qualitatively interpolated between the two known limiting cases.[2] Coming from large distances, the term of the two separated atoms generally splits up. There are two reasons for the splitting: the decrease of the symmetry of the system (spherical symmetry of the atoms, axial symmetry in the system of two centres) generally gives a splitting; as, also, occurs if there is only one electron. If there are more electrons, we get more splitting. That is a typical quantum mechanical effect, which arises from the fact that the forces in

[1] W. Heitler und F. London, *Z. Physik*, **44**, 455, 1927.
F. London, *Z. Physik*, **46**, 455, 1927; **50**, 24, 1928; *Sommerfeld-Festschr.* S. 104, 1928; *Quantentheorie und chemische Bindung*, in *Leipziger Vorträge* (1928), S. 59.
W. Heitler, *Z. Physik*, **47**, 835, **51**, 805, 1928.

[2] F. Hund, *Z. Physik*, **40**, 742; **42**, 93; **43**, 805, 1927; **51**, 759, 1928. For a summary compare Hund's article in *Ergebnisse der exakten Naturwissenschaften*, **8** (will appear in September, 1929).

the system depend on all the electrons in the same manner; the effect has no classical analogy. The terms of two completely separated atoms do not vary, if an electron of the one atom is exchanged with an electron of the other atom (exchange degeneracy); but such a term splits up if the degeneracy disappears, *e.g.*, if the two atoms are no longer completely separated.[3]

We compare now the terms of H_2 and H + H in the lowest states and the terms of the HeH (if existing) and He + H with the terms of the positive ions by the following two cycle-processes.

$$\begin{array}{ccc} & \overset{D'}{\longrightarrow} & \\ H_2^+ & & H + H^+ \\ \uparrow I_M & & \uparrow I_A \\ H_2 & \xrightarrow{D} & H + H \end{array} \qquad \begin{array}{ccc} & \overset{D'}{\longrightarrow} & \\ HeH^+ & & He + H^+ \\ \uparrow I_M & & \uparrow I_A \\ HeH & \xrightarrow{D} & He + H \end{array}$$

The dissociation energy D of the molecule is higher than the dissociation energy D' of the ion if the term value (or ionisation energy) I_M of the molecule is higher than the term value I_A of one of the atoms. The term value of H_2 in the lowest state is expected to differ from that of H in the direction towards the term value of He in the lowest state; we expect $I_M > I_A$ and consequently $D > D'$. The lowest term of H + H splits up into two: a lower singlet and a higher triplet term.[4] They have been calculated by Heitler and London; the result was, that (to a first approximation) the lower state gives binding, the higher not. The term value of the HeH in the lowest state is expected to differ from that of the He + H in the direction towards the term value of Li; we expect $I_M < I_A$ and $D < D'$. It is doubtful whether D is positive or not.

We can assign the responsibility for the characteristic difference between H_2 and HeH to several causes:

(1) The fact that in H_2 (as in He) the two electrons are in equivalent orbits and in HeH the third electron is, according to Pauli's principle, in a higher orbit.

(2) The splitting up of the H + H-term and the absence of any splitting in the case of the He + H-term).[5] Correspondingly, we can assign the responsibility for the difference between the two H_2-terms calculated by Heitler and London [1] to the fact that in He (lower) we have equivalent orbits and in the higher state not; or

(3) That in the lower the *eigenfunction* has no node between the equal nuclei, while there is such a node in the higher state.

We see, there can be *several conditions which are favourable for binding*, and we ought to consider them all. If with (1) we make the difference only of equivalent and not of equivalent orbits, the result is not very fruitful. A more detailed consideration must have regard to the relative distances between the energies of the different orbits. We have only orbits with 2 or 4 electrons, but some of them can lie close together,

[3] The effect of the exchange degeneracy was discovered by Heisenberg; *Z. Physik*, **38**, 411; **39**, 499, 1926; **41**, 239, 1927. The general consequences for the term structure of atoms and molecules were discussed principally by E. Wigner, *Z. Physik*, **40**, 492, 883; **43**, 624; **45**, 601, 1927; by J. v. Neumann and E. Wigner, *ibid.*, **47**, 203; **49**, 73; **51**, 844, 1928; and by E. Wigner and E. E. Witmer, *ibid.*, **51**, 859, 1928.

[4] In the language of term systematics $^1\Sigma$ even, $^3\Sigma$ odd.

[5] S + ^{2}S gives only $^2\Sigma$.

so that we have some similarity, *e.g.*, with the shells of 8-electrons in an atom. This point of view Mulliken [6] has considered, and he found it fruitful in some cases, *e.g.*, in the case of hydrides.

The second suggested cause of the splitting seems very schematical, but it leads to an energetical understanding of London's interpretation of valency. The splitting up of the terms of two separated atoms (or molecules, which can form a more complex molecule) depends not only on the exchange-degeneracy. If, however, we avoid the other influence by considering atoms in S-terms, the splitting up only depends on the multiplicity of the terms of the separated atoms. The higher the multiplicity, the higher the multitude of multiplets which come from the multiplet of the two atoms. The calculations of London and Heitler show that the magnitude of the splitting also increases with the multiplicity. If one of the atoms is in an ^{1}S-state and the other in any S-state, we get no splitting. If, with London, we define the valency of an atom or molecule in a definite (multiplet) state by a number which is one lower than the multiplicity, it follows that higher valency is a cause (but not the only cause) of the larger splitting and therefore of binding. In the case of valency 0, this cause is absent.

The power to enable an atom to form compounds is only one of the essential properties of the empirical conception of valency. The other is the fact that valencies are usually saturated in binding, *i.e.*, that two atoms with the valencies v_1 and v_2 make a molecule with the valency $|v_1 - v_2|$. In some cases London's quantum theoretical conception of valency has the same property. If the molecule has only orbits which are closed with two electrons,[7] and if we consider the lowest states of the separated atoms it is very plausible to suggest that the term with lowest multiplicity coming from the splitting up has the lowest energy. Its multiplicity is $|m_1 - m_2| + 1$, where m_1 and m_2 are the multiplicities of the two atomic terms, its valency therefore is $|v_1 - v_2|$. In more complicated cases, *e.g.*, shells with 4 electrons in the molecule, higher states of the atoms, the result is much more complicated, and we get no general rules.

We know from chemical experience, that the conception of chemical valency does not go far towards explaining binding. We must not be surprised that London's quantum theoretical conception has the same failing. It seems, however, that the two conceptions were the same, *i.e.*, that *London has given a quantum theoretical explanation of the chemical valency by the energies arising from the disappearance of the exchange degeneracy.*

Condition (3) is of some value in the cases where the two others give no result. In some of the higher terms of H_2 coming from H + H we see the terms which are symmetrical to a plane between the nuclei decreasing and giving a binding, while the terms which are antisymmetrical increase.[8] We also can expect that condition (3) has importance in the binding of atoms or molecules in a crystal.

[6] R. S. Mulliken, *Physical Review*, **32**, 186, 1928.

[7] In diatomic molecules the so-called σ-shells are shells with 2, the π-shells can have 4 electrons. In polyatomic molecules we expect only shells with 2 (except very symmetrical cases).

[8] Compare calculations of E. A. Hylleraas, *Z. Physik*, **51**, 150, 1928, and E. C. Kemble and C. Zener, *Physical Rev.*, **33**, 512, 1929.

THE DETAILED ELECTRONIC STRUCTURE OF DIATOMIC MOLECULES, WITH SPECIAL REFERENCE TO CO.

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The interpretation of band spectra is *par excellence*, the road to an understanding of molecular structure. Although it is some 18 years since the first application of the quantum theory was made to molecules, the foundations of the subject have scarcely been laid for more than 10 years. Within the last 3 years progress has been exceedingly rapid, and knowledge has been gained of the *detailed* electronic structure of molecules, in contrast to what may be called the general structure to which the preceding years had contributed so fruitfully. These recent developments are associated especially with two names, those of Professor Hund and Professor Mulliken, both of whom are contributing to the present symposium. It is the purpose of the present paper (*a*) to review briefly our knowledge of general molecular structure gained through the study of electronic band spectra; (*b*) to review the recent contributions of Hund, Mulliken, and others to the detailed electronic structure of molecules; and (*c*) to make further application of these latter methods to a molecule of considerable interest and importance, that of CO.

I. General Molecular Structure.

(1) *Vibration Frequency.*—It is well known that the vibrational energy of an anharmonic oscillator (in which category all diatomic molecules fall) is given by $E^n = h(\omega_0 n - \omega_0 x n^2 + \ldots)$, where n is a quantum number, ω_0 the vibration frequency for oscillations of very small amplitude, and x is a small constant determined by the law of force between the nuclei, I_0, ω_0, etc. The analysis of the gross structure of an electronic band system, in which the various bands are distinguished by transitions between an initial vibrational state n' and a final vibrational state n'', permits of expression of the data by a formula:

$$\nu = \nu_e + (\omega_0' n' - \omega_0' x' n'^2 + \ldots) - (\omega_0'' n'' - \omega_0'' x'' n''^2 + \ldots) \quad (1)^*$$

and from this can be at once inferred the magnitude of the electronic jump ν_e, and the vibration frequency of the molecule in the initial and final electronic states. Thus, $\omega_{n'} = \frac{\partial \nu}{\partial n'}$ and $\omega_{n''} = \frac{\partial \nu}{\partial n''}$.

(2) *Electronic Energy Levels.*—As a rule, several band systems are radiated by any particular molecule, and an analysis of these along similar lines at once makes possible the identification of some of the levels as common to more than one system. In this way, from the various values of ν_e there can be constructed a scheme of electronic

* These expressions conform to the old Quantum Theory. According to the new Quantum Theory $(n + \frac{1}{2})$ must replace n.

energy levels for the molecular emitter. Such a scheme for CO is shown in Fig. 3.

(3) *Energy of Dissociation.*—It is clear from the anharmonic nature of nuclear oscillations that for a certain value of n, $\omega_n = 0$, and this critical value can be deduced when ω_n is known as a function of n for an electronic state. Physically, the process imagined is that of loading the molecule with vibrational energy—the vibrational frequency consequently decreasing—until for a critical number of quanta the atoms fly apart and dissociation results. It is thus possible, as Birge and Sponer have shown, to calculate the energy required to dissociate a molecule when in any of its electronic states. While the value thus calculated for the molecule in its ground state is generally in good agreement with the value determined by quite different methods, the energies of dissociation calculated from the vibrational functions of the various excited electronic levels of the molecule are not necessarily identical, and from these differences vital information can be gained as to the states of the atoms composing the molecule.

(4) *Ionisation Potential.*—If a molecule has sufficient vibrational stability to survive the shock of ionisation, a number of band systems of the ionised molecule may exist (*e.g.*, there are three known systems of CO^+). If D' is the energy of dissociation of the ionised molecule (into an atom and an ion), and D the energy of dissociation of the neutral molecule, while I_a and I_m are the ionisation potentials of the atom and the neutral molecule respectively, then :

$$I_m + D' = D + I_a \quad . \quad . \quad . \quad . \quad (2)$$

Thus, I_m can be deduced from purely spectroscopic data. There are of course other and more accurate methods of determining this quantity, so that the principal usefulness of the above relation is rather to calculate D' where it cannot be otherwise determined.

(5) *Effective Electronic Quantum Numbers.*—If to our scheme of electronic energy levels is added a knowledge of the ionisation level ν_0, we can then deduce the "effective" electronic quantum numbers corresponding to the various electronic levels, on the assumption that the terms are of the Rydberg type. The "effective" quantum numbers will be given by $\sqrt{\frac{R}{\nu_0 - \nu}}$. In the case of the H_2 and the He_2 molecule and to a less extent in some other molecules, series of electronic terms are found, the effective quantum numbers of which differ by unity. This is direct evidence of the similarity of these orbits to those familiar throughout the range of atomic spectra. In the majority of molecules, however, there is distinct evidence of important differences between electronic orbits in molecules and atoms. Thus, for example, a series of ^1S molecular terms may have effective quantum numbers, the differences between which are irregular and fractional. A clue to the nature of these facts is found in the recent work of Mulliken, which is discussed in Part II. of this paper.

(6) *Moment of Inertia and Inter-nuclear Distance.*—The field of fine structure analysis, which is concerned with the rotational transitions taking place in a molecule, yields a wealth of further information. It is well known that the three types of branches occurring in band structure, which are usually designated P, Q, and R, are accounted for respectively by transitions $j - 1 \rightarrow j$, $j \rightarrow j$, and $j + 1 \rightarrow j$ of a quantum number j, where $jh/2\pi$ is the total angular momentum of the molecule. Thus, by a proper assignment of j-values to the lines of a band, and the subsequent

application of mathematical methods based on the so-called combination principle, the moments of inertia of the molecule in both the initial and final states of the transition can be evaluated. From these, if the masses of the atoms in the molecule are known, the inter-nuclear distance r can be calculated thus :

$$I = (1{\cdot}650 \times 10^{-24}) \frac{m_1 m_2}{m_1 + m_2} \cdot r^2 \quad . \quad . \quad . \quad . \quad (3)$$

In favourable cases a knowledge of molecular sizes can in this way be obtained to an accuracy of about ·001 Ångström Units.

(7) *The Quantum Numbers j, m, ϵ, i.*—The rotational quantum number m measures, in units of $\frac{h}{2\pi}$, the *nuclear* angular momentum of the molecule; ϵ and i are two quantum numbers which usually have small values, such as 0, $\frac{1}{2}$, 1, 2, etc., and measure respectively the components of *electronic* angular momentum perpendicular to, and parallel to, the inter-nuclear axis. The total quantum number is clearly related to these by the formula first suggested by Kramers and Pauli :

$$j^2 = (m \pm \epsilon)^2 + i^2 \quad . \quad . \quad . \quad . \quad (4)$$

For even-valence-electron molecules j is half-integral, for odd molecules it takes integral values. This is true on the basis of the old Quantum Theory : on the new Quantum Theory $j(j + 1)$ replaces j^2. Writing this $[(j + \frac{1}{2})^2 - \frac{1}{4}]$, it is clear that the new j-values will be $\frac{1}{2}$ less than the old ones. In the process of analysis of band structure by the combination principle, the values of ϵ' and ϵ'' (for the initial and final states) can be evaluated along with other molecular constants. The quantum numbers i' and i'' cannot, however, be determined directly by analysis. Mulliken has shown that it is possible arbitrarily to assign i-values to both initial and final molecular states by determination of the number of missing lines in the neighbourhood of the band origins. Since from (4) $m = \sqrt{j^2 - i^2} \mp \epsilon$, it follows that $j_{\min}$ clearly must be greater than i to make m real. Knowing the value of i, the nature of the electronic state, such as S, P, D, etc., is, as we shall see later, at once determinable.

(8) *Reciprocal Energy Relations within the Molecule.*—In the elemen tary treatment of a molecule as a *rigid* rotating dipole, the nuclear rotational energy is expressed by the single term Bm^2 where $B = \frac{h}{8\pi^2 I}$. Higher-power terms arise when the " elasticity " of the molecule is taken into account, and in general, the nuclear rotational energy is given by :

$$F(m) = Bm^2 + Dm^4 + Fm^6 + Hm^8 + \ldots \quad . \quad . \quad (5)$$

It is clear that no dynamical treatment which regards the electronic, vibrational, and rotational energy changes in a molecule as taking place independently can be more than a first approximation to the truth. There will, in practice, be contributions arising from mutual effects, such as of vibration on rotation, rotation on vibration, rotation on electronic motion, etc., and many of these relationships are of considerable theoretical importance.

(9) *Law of Force.*—From a knowledge of the coefficients, B, D, F, and H, it is possible to evaluate the constants of the internuclear law of force. This binding force must be of the form :

$$F = k_1(r - r_0) + k_2(r - r_0)^2 + k_3(r - r_0)^3 + \ldots$$

where r represents the inter-nuclear separation in general, and r is the equilibrium value. Birge has derived expressions for k_1, k_2, k_3, etc., in terms of B, D, F, and H. The best method of evaluating the constants k makes use of both vibrational and rotational data, and Kemble and others have derived formulæ by which this can be done. A knowledge of the law of force and its variations in the different electronic states of the molecule is clearly of considerable importance. It is intimately related to problems connected with the structure and stability of the molecule, and it is a controlling factor in the distribution of intensity among the bands of each system emitted.

(10) *Molecular and Atomic Electronic Levels.*—In many respects, though not in all respects, molecular electronic states have a close resemblance to atomic states. As in the latter, we find multiplicity such as ^3S, ^2P, ^5D, etc., the general laws governing which are the same in both cases. Thus a given molecule can exhibit only odd or only even multiplicities, but not both. Molecules having an even number of electrons exhibit odd multiplicity, and molecules with an odd number of electrons show even multiplicity. The molecules BeF, BO, CN, CO^+, N_2^+, all of which have 13 electrons, give a system of doublet electronic levels which are very similar to those of the "corresponding" Na atom. If, as is probable in these molecules, two electrons are closely bound to each nucleus—(the atomic K shells)—there will be 9 electrons forming an external structure as in the Na atom. Not only does the general disposition of molecular electronic levels bear a certain measure of resemblance to that in the "corresponding" atom, but the magnitude of the multiplet separations is of the same order. In the same way, the electronic schemes of CO and N_2 are similar in some respects to Mg, and those of NO and O_2 are similar to the Al atom. It was analogies such as these which led Birge, in 1926, to make the generalisation that "the energy levels associated with the valence electrons of molecules agree in all essential respects with those associated with the valence electrons of atoms." While the correspondence mentioned has proved a valuable and useful conception, it is now generally recognised that this statement is too wide. In several molecules which have been investigated sufficiently, there are found to be levels which have no counterpart in the corresponding atom. Certain features which would appear at first sight to be minor differences between the electronic levels of atoms and molecules, have, in fact, proved important points of departure for a detailed knowledge of the electronic structure of molecules. These statements will be amplified later.

(11) *Multiplicity in Molecular Electronic Levels.*—In atomic spectra the levels of an electronic multiplet are characterised by particular j-values, where j, here the inner quantum number, is obtained by vector summation of l, the electronic orbital angular momentum, and s, the electronic spin angular momentum. The orientations of the spin are controlled by the intra-atomic magnetic field which, for a given state of the atom is fixed. The resultant magnetic field in a molecule is, however, more complicated in its origin, depending to some extent on nuclear rotation. From this arise electronic multiplets whose width is variable, being, in fact, a function of j, the rotational quantum number.

Owing to the strong electric field along the inter-nuclear axis, the l vector in a molecule will be in rapid precession about this axis. The corresponding quantum number i_l represents the component of l along this axis. In the rotationless molecule i_l probably gives rise to the sole

magnetic field, and this controls the orientation of s. The spin s will therefore precess about the inter-nuclear axis giving rise to the corresponding quantum number i_s. The quantum number i of Section (7) is thus generalised by this conception, and is given by $i = i_l + i_s$. The nature of a molecular electronic state is determined by i_l: $S(i_l = 0)$, $P(i_l = 1)$, $D(i_l = 2)$, etc. The term multiplicity is, of course, given by $2s + 1$, while the sub-levels of a multiplet are distinguished by different i-values. The quantum numbers i, i_l, i_s, therefore, play analogous parts in this instance, to j, l, and s of atomic spectra. This is Hund's case (a). When the molecule is rotating there may be also a magnetic field perpendicular to the inter-nuclear axis, and the spin is then quantised with respect to the resultant magnetic field along the j_l axis (j_l is the resultant of m and i_l). The corresponding quantum number may appropriately be called j_s, where now $j = j_l + j_s$. This is Hund's case (b), and under these conditions j, j_l, and j_s, are the counterpart of j, l, and s of atomic spectra. These are two extremes which are in practice approached as limiting cases. It will be appreciated, however, that the actual magnitude of j is not in itself the controlling factor, but that the specific structure of the molecule, and in particular the nature and strength of the electronic-rotational couplings will largely govern the facility of transition from one extreme case to the other. Passing from low to high j values, there is usually a gradual orientation of the axis about which s is quantised, from parallelism to the inter-nuclear axis to a position approximately perpendicular to it. In the particular case of S states $i_l = 0$. There is no resulting magnetic field along the inter-nuclear axis, so that the spin vector necessarily orientates perpendicular to this axis, and s appears as ρ ($\rho = \pm \epsilon$ of equation (4)). If the values of ϵ were always exactly integers or half-integers, there would not arise any multiplication of the band structure, but component lines would exhibit a precise superposition on others. Secondary causes contribute, however, to slight departures from these values, and hence there arises so-called ρ-type doubling. In P and D states where $i_l > 0$, there is also so-called i-type doubling which can be expressed by two slightly differing values of the moment of inertia. It is frequently accompanied also by small secondary ρ^s. The sub-levels which are usually distinguished by subscripts A and B, thus give terms of the types:

$$F_A(j) = B_A[\sqrt{j^2 - i^2} - \rho_A]^2 + \ldots, \quad F_B(j) = B_B[\sqrt{j^2 - i^2} - \rho_B]^2.$$

The properties of these terms and the laws governing transitions to and from them have been worked out in detail by Mulliken and others.[1]

II. Detailed Molecular Structure.

The work of Hund on line spectra has provided a theoretical basis for the systematisation of even the most complicated atomic spectra. Given an atom with a specified electronic configuration, it is possible to predict the manifold of spectral terms which should arise, and conversely, it is possible to infer from analysis of a spectrum the probable atomic configuration which produces it. The recent work of Hund, Mulliken, Heitler, and London, and others, is a development of similar methods for molecular spectra, and a detailed knowledge has been obtained of the various electronic orbits in a number of typical diatomic molecules. The molecular electronic configuration must, of course, be satisfactorily

[1] *Vide Physical Rev.*, **28**, 481, 1926, and seven subsequent papers.

correlated with that of the individual atoms composing it, and both the energy of dissociation of the molecule and the precise electronic states of the atomic products of dissociation must be in harmony with this structure.

Molecular Quantum Numbers and Notation.

In an atom a particular electron is described by three quantum numbers, n, l, and s ($= \frac{1}{2}$), and the resultant state of the atom, such as, for example, $^2S_{\frac{1}{2}}$, $^3P_2$, etc., is deduced by compounding these individual quantum numbers to get a resultant l, s, and j, by the methods developed by Hund. To a particular electron in a *molecule* (distinguished by the subscript τ), four quantum numbers must be assigned, n_τ, l_τ, i_{l_τ}, and s_τ ($= \frac{1}{2}$), while the molecular state, as a whole, is given by l, i_l, s, and i ($= i_l + i_s$). The latter is, of course, strictly true for the vibrationless rotationless molecule under the conditions of Hund's case (*a*). Otherwise, as in case (*b*), i_l is no longer in entire magnetic control of s, so that i_s (and i) are meaningless, and s is quantised with respect to the j_l axis, giving the quantum number j_s. The following notation is suggested by Hund for the description of molecular structure. Small letters s, p, d, f, etc., are retained for the *individual* electrons to denote states corresponding to $l_\tau = 0, 1, 2, 3$, respectively; similarly, σ, π, δ, ϕ, etc., are used to denote the i_{l_τ} values 0, 1, 2, 3, etc. Capital letters S, P, D, F, etc., refer to the molecule *as a whole*, denoting respectively $l = 0, 1, 2, 3$, etc.; similarly, Σ, Π, Δ, Φ, correspond to $i_l = 0, 1, 2, 3$, etc. Thus, as examples, the unexcited states of the C atom and the C_2 molecule,[2] would be written as follows:

$(1s)^2(2s)^2(2p)^2 : {}^3P$ . . . . . (C atom)
$(1s\sigma)^2(2p\sigma)^2(2s\sigma)^2(3p\sigma)^2(2p\pi)^3(3s\sigma) : {}^3\Pi_i{}^{\mathrm{P}}$ . . (C$_2$ molecule).[3]

The order in which the electrons are placed is that which observation indicates is of diminishing binding energy. In molecular structure i_l plays a part largely corresponding to l in atomic spectra: it determines, for example, the nature of the molecular states, such as Σ, Π, Δ, etc. The rôle of l in molecular structure is subsidiary to that of i_l, and effects a further classification of states which have the same i_l. In the above example, $^3\Pi^{\mathrm{P}}$, the ground state of the C_2 molecule, indicates $s = 1$, $l = 1$, and $i_l = 1$. The first excited state

$$(1s\sigma)^2(2p\sigma)^2(2s\sigma)^2(3p\sigma)(2p\pi)^3(3s\sigma)^2 : {}^3\Pi_i{}^{\mathrm{D}},$$

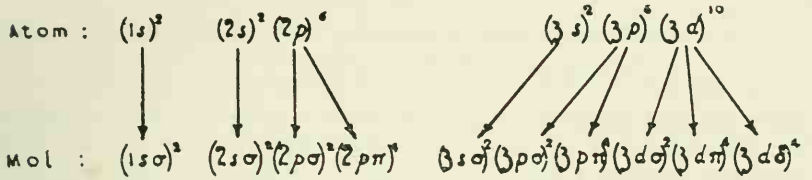
which is 2·39 volts higher, correspond to $s = 1$, $l = 2$, $i_l = 1$. We mention this to illustrate two features peculiar to molecular states: (1) While there are two $^3\Pi$ levels in the above molecule, the counterpart is a single state in the corresponding atom Neon. It is thus apparent that in general there are more electronic levels in molecules than there are in the corresponding atoms, within the same range. (2) The electronic transition $(3s\sigma) \rightarrow (3p\sigma)$ is responsible for a well-known band system, the "Swan" bands. Neither n_τ nor i_{l_τ} changes, but $\Delta l_\tau = +1$. This electronic transition in the C_2 molecule is thus of the "X-ray" rather than the optical type, and apart from the H_2 and He_2 molecules, and a few other molecules of a loosely-bound type, such transitions are

[2] *Roy. Soc. Proc.*, A. **124**, 668, 1929.
[3] The subscript i denotes that the molecular state $^3\Pi$ is inverted.

the rule rather than the exception. It follows that while a number of molecular terms of a particular type, such as $^1\Sigma$, for example, may be found by analysis of a spectrum, it is not to be expected that these will all fit into a Rydberg series.

Molecular Electronic Shells and States.

It is well known that the Pauli principle, which postulates the uniqueness of the condition of each electron, limits the number of electrons in an atomic shell of a particular type to $2(2l + 1)$. The same principle is applied to molecules, except that now it is not the (l_τ, s_τ) combination, but that of $(l_\tau, i_{l\tau}, s_\tau)$ which must be unique. The successive types of closed shells in atoms and molecules are, therefore, as given below:



The atomic closed shells are characterised by $l = 0$, $s = 0$, and the molecular closed shells by $i_l = 0$, $s = 0$. The dissociation of the atomic shells which takes place when the atom becomes part of a molecule is indicated by the arrows. There is a measure of stability, though it is less than that of a closed shell, about a shell of two electrons for which $s = 0$. The formation of such shells-of-two is the physical basis of the valence bonds produced when two or more atoms unite to give a molecule. According to London's theory of valency, the formation of one or more such shells is essential to molecule formation. Mulliken, however, regards this as incidental, and holds that the essential condition is a sufficiently low "promotion energy" of the electrons. By "promotion" of an electron is meant an increase of its principal quantum number n (accompanied usually, though not inevitably, by a consequent change $\Delta l = \pm 1$). Such promotions are necessary in the formation of a molecule from atoms, in order to satisfy the demands of the Pauli principle. An example will make this clear. Fig. 1 illustrates a conceivable mode of formation of the normal C_2 molecule from two carbon atoms. Promotions are indicated by dotted lines.

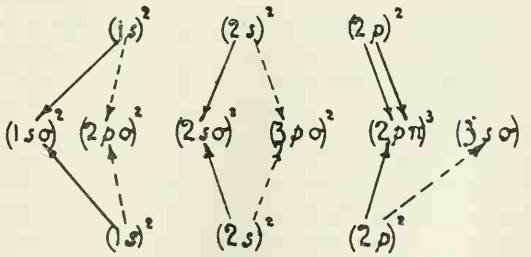


FIG. 1.

The most stable state of the molecule, according to Mulliken, is that of minimum promotion energy. As a general rule, it would appear that electrons in unpromoted orbits exert a strong bonding power on the molecule, while those in promoted orbits have a weak or negative bonding

power. This is reflected in the various values of D^v, the energy of dissociation of the molecule in its various states. Just as in atomic spectra, those electrons which are not in closed shells determine the resulting atomic state, so also in molecules. Algebraic summation of the i_{l_τ} and i_{s_τ} values in molecules replaces vector summation of the l_τ and s_τ values in atoms. One or two examples will illustrate this. Suppose the electrons external to closed shells are $(A\pi)^2$ where A stands for some value of n_τ and l_τ. Each electron has thus four possible states given by :

$$\begin{matrix} i_{l_\tau} : + 1 & - 1 & + 1 & - 1 \\ i_{s_\tau} : + \tfrac{1}{2} & - \tfrac{1}{2} & - \tfrac{1}{2} & + \tfrac{1}{2} \end{matrix}$$

From these states we can obtain ${}^4C_2$, *i.e.*, six possible sums, *viz.*,

$$\begin{matrix} i_l : 2 & - 2 & 0 & 0 & 0 & 0 \\ i_s : 0 & 0 & 1 & 0 & - 1 & 0 \end{matrix}$$

These fall into three groups, corresponding to the states :

$$i_l = 2,\ s = 0,\ ({}^1\Delta)\ ;\quad i_l = 0,\ s = 1\ ({}^3\Sigma)\ ;\quad i_l = 0,\ s = 0,\ ({}^1\Sigma).$$

If the external electrons differ in their n_τ or l_τ values, say $(A\pi)(B\pi)$, then any one of the four pairs of $(i_{l\tau}, i_{s\tau})$ values of one electron may be taken with any one pair of the other electron. There are thus 16 possible (i_l, i_s) combinations, and the additional molecular state ${}^3\Delta$ appears. By such methods the molecular states resulting from any given detailed electronic configuration can be determined. Table I. is a compilation

TABLE I.

External Electrons.	Molecular States.	External Electrons.	Molecular States.
$(A\sigma)$	${}^2\Sigma$	$(A\pi)^3\,(B\pi)$	${}^3\Delta_i,\ {}^3\Sigma,\ {}^1\Delta,\ {}^1\Sigma$
$(A\sigma)(B\sigma)$	${}^3\Sigma,\ {}^1\Sigma$	$(A\pi)^2(B\pi)^2$	${}^5\Sigma,\ {}^3\Sigma,\ {}^1\Sigma,\ {}^3\Delta,\ {}^3\Sigma,\ {}^1\Gamma,\ {}^1\Delta,\ {}^1\Sigma$
$(A\pi)$	${}^2\Pi$	$(A\pi)^3(B\pi)^2$	${}^4\Pi_i,\ {}^2\Phi,\ {}^2\Pi,\ {}^2\Pi_i,\ {}^2\Pi_i$
$(A\pi)^2$	${}^3\Sigma,\ {}^1\Delta,\ {}^1\Sigma$	$(A\pi)^3(B\pi)^3$	${}^3\Delta_i,\ {}^3\Sigma,\ {}^1\Delta,\ {}^1\Sigma$
$(A\pi)(B\pi)$	${}^3\Delta,\ {}^3\Sigma,\ {}^1\Delta,\ {}^1\Sigma$	$(A\pi)(B\delta)$	${}^3\Phi,\ {}^3\Pi,\ {}^1\Phi,\ {}^1\Pi$
$(A\sigma)(B\pi)$	${}^3\Pi,\ {}^1\Pi$	$(A\pi)^2(B\delta)$	${}^4\Delta,\ {}^2\Delta_i,\ {}^2\Gamma,\ {}^2\Sigma,\ {}^2\Delta$
$(A\sigma)(B\pi)^2$	${}^4\Sigma,\ {}^2\Sigma,\ {}^2\Delta,\ {}^2\Sigma$	$(A\pi)^3(B\delta)$	${}^3\Phi,\ {}^3\Pi,\ {}^1\Phi,\ {}^1\Pi$
$(A\pi)^3$	${}^2\Pi_i$	$(A\delta)^2$	${}^3\Sigma,\ {}^1\Gamma,\ {}^1\Sigma$
$(A\sigma)(B\pi)^3$	${}^3\Pi_i,\ {}^1\Pi$	$(A\delta)^3$	${}^2\Delta_i$
$(A\pi)^2(B\pi)$	${}^4\Pi,\ {}^2\Pi,\ {}^2\Phi,\ {}^2\Pi_i,\ {}^2\Sigma$	$(A\sigma)(B\delta)$	${}^3\Delta,\ {}^1\Delta$

of such states for some of the simpler molecular structures. This is similar to a list derived by Mulliken, but the most recent nomenclature is used. (A subscript i indicates that the multiplet is inverted. We are now led to consider as a key to the detailed structure of any particular molecule, what happens when the two constituent atoms are brought together in the process of formation. This problem is clearly fundamental to synthetic chemistry.

The Mechanism of Molecular Formation.

At the beginning of the previous section, an apparently arbitrary application of the Pauli principle was made to molecular configurations. This was based essentially on Hund's conception of a molecule as an interpolation between two limiting cases : (1) two separate atoms ; and

(2) the "united-atom." The "united-atom" may be imagined as produced by bringing the two constituent atoms so close together as to fuse the nuclei. To each simple molecule there corresponds such an atom, although its production by a synthesis such as the above is purely an imaginary process. Thus, Mg is the united-atom corresponding to C_2, Al corresponds to CN, Si to CO, etc. The quantum number assignments in the molecule should be similar to those of the united-atom in a non-uniform axially symmetrical electric field: the conditions for a Stark effect. Such a field is actually present in the molecule, due to the two atomic nuclei, the line joining the nuclei being the axis of symmetry. The resemblance of the molecule to the united-atom in an electric field has been already utilised in the assignment of quantum numbers, the determination of molecular shells, etc. We now proceed to consider the correlation, such as is found in the processes of molecular synthesis and dissociation, with the constituent atoms.

We may gain insight into molecular structure by taking the separate atoms, introducing them into an electric field of appropriate strength and then bringing them together (removing the artificial electric field, as it is replaced increasingly by the inter-nuclear field). Our immediate enquiry is therefore into the quantum states of an atom in an electric field. These are clearly dependent on the strength of the field. We may first remind ourselves by Fig. 2 of the various magnetic couplings in an atom in the absence of the field. The l_τ vectors are coupled to give a resultant l, the s_τ vectors to give a resultant s, while l and s are coupled to give j the inner quantum number. Hund has distinguished four different stages corresponding to increasing field strength :—

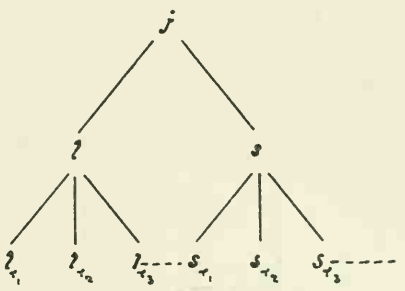


FIG. 2.

(1) A weak field in which none of the couplings are broken down. The j is quantised with respect to the field axis, giving a quantum number i.

(2) A moderate field in which the coupling between l and s is broken down: l and s are then separately space-quantised with respect to the field, giving i_l and i_s.

(3) A strong field in which the individual l_τ are couplings broken down. The original l of the fieldless atom disappears, and each l_τ is quantised individually, giving an i_{l_τ}, while $\Sigma i_{l_\tau} = i_l$. The spin s still remains intact, and is quantised to give i_s.

(4) A very strong field approximating to the Stark effect. The s_τ couplings are not broken down at any field intensity. The quantum numbers existing at these various stages may be summarised:

Case 1: $l_\tau, s_\tau, l, s, j, i$.
Case 2: $l_\tau, s_\tau, l, s, i_l, i_s$ $(i = i_l + i_s)$.
Case 3: $l_\tau, s_\tau, s, i_{l_\tau}, i_s$ $(i_l = \Sigma i_{l_\tau})$, $(i = i_l + i_s)$.
Case 4: $s_\tau, s, i_{l_\tau}, i_s$ $(i_l = \Sigma i_{l_\tau})$, $(i = i_l + i_s)$.

It is not possible to draw any hard and fast line between the various stages, but it would appear that the conditions of Case 3 approximate to reality in a very large number of molecules. In some loosely-bound

molecules, such as Na_2, K_2, NaK, and in hydrides, such as HgH, we probably have Case (2), and possible in some instances Case (1). In hydrogen (H_2) the multiplicity of states suggests Case (4) may be approached.

Returning to consideration of the typical case, it results that in the field l_τ is quantised to give i_{l_τ}, which may take the values l_τ, $l_\tau - 1$, $l_\tau - 2$, . . . $-(l_\tau - 2)$, $-(l_\tau - 1)$, $-l_\tau$, and i_s similarly takes values

TABLE II.

Atom.	Without Field.				With Field.				
	State.	Term Value.	l.	s.	i_l.	i_s.	State.	Configuration.	Number of Components.
He	^3S	38,455	0	1	0	$\pm 1, 0$	$^3\Sigma^S$	σ^2	3
	^1S	32,032	0	0	0	0	$^1\Sigma^S$	σ^2	1
	^3P	29,223	1	1	0	$\pm 1, 0$	$^3\Sigma^P$	σ^2	3
					± 1	$\pm 1, 0$	$^3\Pi^P$	$\sigma\pi$	6
	^1P	27,175	1	0	0	0	$^1\Sigma^P$	σ^2	1
					± 1	0	$^1\Pi^P$	$\sigma\pi$	2
Li	^2S	43,486	0	$\frac{1}{2}$	0	$\pm \frac{1}{2}$	$^2\Sigma^S$	σ^3	2
	^2P	28,582	1	$\frac{1}{2}$	0	$\pm \frac{1}{2}$	$^2\Sigma^P$	σ^3	2
					± 1	$\pm \frac{1}{2}$	$^2\Pi^P$	$\sigma^2\pi$	4
Be	^1S	75,180	0	0	0	0	$^1\Sigma^S$	σ^4	1
	^3P	53,213	1	1	0	$\pm 1, 0$	$^3\Sigma^P$	σ^4	3
					± 1	$\pm 1, 0$	$^3\Pi^P$	$\sigma^3\pi$	6
	^1P	32,615	1	0	0	0	$^1\Sigma^P$	σ^4	1
					± 1	0	$^1\Pi^P$	$\sigma^3\pi$	2
B	^2P	$668\begin{cases}40\\24\end{cases}$	1	$\frac{1}{2}$	0	$\pm \frac{1}{2}$	$^2\Sigma^P$	σ^5	2
					± 1	$\pm \frac{1}{2}$	$^2\Pi^P$	$\sigma^4\pi$	4
	^2S	26,800	0	$\frac{1}{2}$	0	$\pm \frac{1}{2}$	$^2\Sigma^S$	σ^5	2
C	^3P	$\begin{cases}91{,}017\\91{,}002\\90{,}975\end{cases}$	1	1	0	$\pm 1, 0$	$^3\Sigma^P$	$\sigma^4\pi^2$	3
					± 1	$\pm 1, 0$	$^3\Pi^P$	$\sigma^5\pi$	6
	^1D	81,312	2	0	0	0	$^1\Sigma^D$	σ^6	1
					± 1	0	$^1\Pi^D$	$\sigma^5\pi$	2
					± 2	0	$^1\Delta^D$	$\sigma^4\pi^2$	2
	^1S	69,860	0	0	0	0	$^1\Sigma^S$	$\sigma^4\pi^2$	1
N	^4S	117,345	0	$1\frac{1}{2}$	0	$\pm 1\frac{1}{2}, \pm \frac{1}{2}$	$^4\Sigma^S$	$\sigma^5\pi^2$	4
	^2D	98,143	2	$\frac{1}{2}$	0	$\pm \frac{1}{2}$	$^2\Sigma^D$	$\sigma^5\pi^2$	2
					± 1	$\pm \frac{1}{2}$	$^2\Pi^D$	$\sigma^6\pi$	4
					± 2	$\pm \frac{1}{2}$	$^2\Delta^D$	$\sigma^5\pi^2$	4
	^2P	88,537	1	$\frac{1}{2}$	0	$\pm \frac{1}{2}$	$^2\Sigma^P$	$\sigma^5\pi^2$	2
					± 1	$\pm \frac{1}{2}$	$^2\Pi^P$	$\sigma^4\pi^3$	4
O	^3P	$109\begin{cases}607\\674\\833\end{cases}$	1	1	0	$\pm 1, 0$	$^3\Sigma^P$	$\sigma^6\pi^2$	3
					± 1	$\pm 1, 0$	$^3\Pi^P$	$\sigma^5\pi^3$	6
	^1D	$\begin{cases}?\\17924{\cdot}7\\?\end{cases}$	2	0	0	0	$^1\Sigma^D$	$\sigma^6\pi^2$	1
					± 1	0	$^1\Pi^D$	$\sigma^5\pi^3$	2
					± 2	0	$^1\Delta^D$	$\sigma^6\pi^2$	2
	^1S	?	0	0	0	0	$^1\Sigma^S$	$\sigma^4\pi^4$	1
F	^2P	138,000 ?	1	$\frac{1}{2}$	0	$\pm \frac{1}{2}$	$^2\Sigma^P$	$\sigma^5\pi^4$	2
					± 1	$\pm \frac{1}{2}$	$^2\Pi^P$	$\sigma^6\pi^3$	4
	^4P	?	1	$1\frac{1}{2}$	± 1	$\pm 1\frac{1}{2}, \pm \frac{1}{2}$	$^4\Pi^P$	$\sigma^6\pi^3$	8
					0	$\pm 1\frac{1}{2}, \pm \frac{1}{2}$	$^4\Sigma^P$	$\sigma^5\pi^4$	4

s, $s-1$, $s-2$, . . . $-(s-2)$, $-(s-1)$, s. Hence, for the atom-in-the-field there exist a series of quasi-molecular states, in describing which the molecular notation is employed. In Table II. the quasi-molecular states have been given for the atoms of the first short period. The column headed configuration summary gives the detailed i_{l_τ} values of the atom. Thus, for example, the C-atom in the $^3\Pi^p$ state is, written in full: $(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)$. The n_τ and l_τ values are not retained in the configuration summary: in any case, some of these would be altered by promotion when the molecule was formed by adding the atoms. The column headed "number of components," is the product of the numbers of i_l and i_s values. From such a table the states of a molecule composed of two of these atoms can easily be determined. As an example, the states of the BeO molecule have been deduced, and are listed in Table III. Only one band system of this molecule is at present

TABLE III.

MOLECULAR STATES OF BeO.

Atomic States.		Molecular States.	Configuration Summary.	Atomic States.		Molecular States.	Configuration Summary.
Field Absent.	States in Field.			Field Absent.	States in Field.		
Be. O.	Be. O.			Be. O.	Be O.		
$^1S + {}^3P_i$	$^1\Sigma + {}^3\Sigma$	$^3\Sigma$	$\sigma^{10}\pi^2$		$^3\Sigma + {}^1\Delta$	$^3\Delta$	$\sigma^{10}\pi^2$
	$^1\Sigma + {}^3\Pi$	$^3\Pi$	$\sigma^9\pi^3$		$^3\Pi + {}^1\Sigma$	$^3\Pi$	$\sigma^9\pi^3$
$^3P + {}^3P_i$	$^3\Sigma + {}^3\Sigma$	$^5\Sigma, {}^3\Sigma, {}^1\Sigma$	$\sigma^{10}\pi^2$		$^3\Pi + {}^1\Pi$	$^3\Delta, {}^3\Sigma$	$\sigma^8\pi^4$
	$^3\Sigma + {}^3\Pi$	$^5\Pi, {}^3\Pi, {}^1\Pi$	$\sigma^9\pi^3$		$^3\Pi + {}^1\Delta$	$^3\Pi, {}^3\Phi$	$\sigma^9\pi^3$
	$^3\Pi + {}^3\Sigma$	$^5\Pi, {}^3\Pi, {}^1\Pi$	$\sigma^9\pi^3$	$^1P + {}^1D$	$^1\Sigma + {}^1\Sigma$	$^1\Sigma$	$\sigma^{10}\pi^2$
		$^{5,3,1}\Delta$,					
	$^3\Pi + {}^3\Pi$	$^{5,3,1}\Sigma$	$\sigma^8\pi^4$		$^1\Sigma + {}^1\Pi$	$^1\Pi$	$\sigma^9\pi^3$
$^1P + {}^3P$	$^1\Sigma + {}^3\Sigma$	$^3\Sigma$	$\sigma^{10}\pi^2$		$^1\Sigma + {}^1\Delta$	$^1\Delta$	$\sigma^{10}\pi^2$
	$^1\Sigma + {}^3\Pi$	$^3\Pi$	$\sigma^9\pi^3$		$^1\Pi + {}^1\Sigma$	$^1\Pi$	$\sigma^9\pi^3$
	$^1\Pi + {}^3\Sigma$	$^3\Pi$	$\sigma^9\pi^3$		$^1\Pi + {}^1\Pi$	$^1\Delta, {}^1\Sigma, {}^1\Sigma$	$\sigma^8\pi^4$
	$^1\Pi + {}^3\Pi$	$^3\Delta, {}^3\Sigma$	$\sigma^8\pi^4$		$^1\Pi + {}^1\Delta$	$^1\Pi, {}^1\Phi$	$\sigma^9\pi^3$
$^1S + {}^1D$	$^1\Sigma + {}^1\Sigma$	$^1\Sigma$	$\sigma^{10}\pi^2$	$^1S + {}^1S$	$^1\Sigma + {}^1\Sigma$	$^1\Sigma$	$\sigma^8\pi^4$
	$^1\Sigma + {}^1\Pi$	$^1\Pi$	$\sigma^9\pi^3$	$^3P + {}^1S$	$^3\Sigma + {}^1\Sigma$	$^3\Sigma$	$\sigma^8\pi^4$
	$^1\Sigma + {}^1\Delta$	$^1\Delta$	$\sigma^{10}\pi^2$		$^3\Pi + {}^1\Sigma$	$^3\Pi$	$\sigma^7\pi^5$
$^3P + {}^1D$	$^3\Sigma + {}^1\Sigma$	$^3\Sigma$	$\sigma^{10}\pi^2$	$^1P + {}^1S$	$^1\Sigma + {}^1\Sigma$	$^1\Sigma$	$\sigma^8\pi^4$
	$^3\Sigma + {}^1\Pi$	$^3\Pi$	$\sigma^9\pi^3$		$^1\Pi + {}^1\Sigma$	$^1\Pi$	$\sigma^7\pi^5$

known, and analysis definitely shows this to be $^1\Sigma \rightarrow {}^1\Sigma$. It is not certain which of the $^1\Sigma$ states of Table III. are to be identified with these two known states. A long—and probably not very reliable—extrapolation of the vibrational data of the BeO system, gives for the energy of dissociation in the initial and final states 10·1 volts and 5·75 volts respectively. This difference $(35200 \cdot \nu)$—which may be considerably in error—may correspond with the $(^1S - {}^1P)$ interval of the Be atom, and if so, it would appear that the normal BeO molecule is derived from ^1S (Be) and ^1D (O), while the known excited state is from ^1P (Be) and ^1D (O). Both are $\sigma^{10}\pi^2$ configurations, and the electronic transition in this case is probably $(3d\sigma) \rightarrow (3p\sigma)$.

It will be noted that in forming the molecule from the two atoms, the configuration, *e.g.*, $\sigma^{10}\pi^2$ in the above case, is derived by addition of the field-configurations of the two atoms. This is referred to as the i_{l_τ}-conservation rule. In addition, it may be remarked that none of the

original components of the atomic states are lost in the synthesis. There are, for example, 5 components from the ^1D oxygen atom, and one from the ^1S beryllium atom : these 5 combinations reappear in the molecular states $^1\Sigma$, $^1\Pi$, and $^1\Delta$. Again, there are three components from the ^1P beryllium atom, so that when united with 5 components of $^1\Delta$ oxygen, there should result 15 components among the molecular states. These are all found in Table III.

It will be apparent from the above simple case of BeO, that compared with the number of observed states, a great many theoretically possible molecular states can be derived. The selection of the correct structure for the observed states is, therefore, not always easy. As already indicated, a knowledge of the vibrational energy of dissociation for the known states is of very great value : unfortunately, this is not always known. Additional evidence can be obtained from such facts as the sizes of the molecule, and also the multiplet separations (which should diminish rapidly with increasing n). A number of selection rules are also available for assistance in deciding the probability of transitions between the proposed states. Unfortunately, again, not all of these are of strictly general application, largely because different molecules may fall in the various categories (Cases 1 to 4) already described. The selection rule $\Delta i_l = \pm 1, 0$ is strict. The rule $\Delta s = 0$ is usual, but may occasionally be suspended for a very strong $i_l : s$ coupling (Hund's case (a)). The rule $\Delta l_\tau = \pm 1$ appears to be generally true—as in atoms—except in case (4) previously mentioned. The rule $\Delta i_{l_\tau} = \pm 1, 0$ is true for Case (3), but not necessarily in Cases (2) or (1).

The methods summarised above have been developed and applied in recent papers by Mulliken to some thirty of the simplest diatomic molecules. Full details of the structures determined have been tabulated in these papers.

In concluding this section, it may be appropriate to refer back to remarks made in the first part of this paper on the departure in certain vital points of the nature of the electronic levels of some simple molecules from those of the "corresponding atom." The departure referred to is, that the $^2\Pi$ levels of CN, N_2, CO, BO, etc., are *inverted*, while those of the "corresponding atom" of sodium are normal. This involves a very different electronic configuration ; the above molecules must have an incomplete shell of π-electrons (lacking one electron), while Na has one p-electron outside closed shells. This is now, of course, intelligible on the basis of the molecular electronic shells already described : these, we have seen are quite different from atomic shells.

III. The CO Molecule.

Electronic Levels and Band Systems.

Apart from H_2 and He_2, more levels are known for this molecule than for any other. At least 16 band systems are now definitely attributable to the neutral CO molecule, and three more are known for the CO^+ ion. Fig. 3 is a scale diagram, showing the known levels and the observed transitions for the neutral CO molecule. It should be consulted in connection with the key : the reference there given is to a paper embodying some of the most recent work on each system, which therefore gives references to earlier papers. The electronic term values appended to each level are approximate values only, and in some cases are doubtless considerably in error. The nature of the levels is also given. A "?"

indicates that this is unknown, or very uncertain, and the position of such levels in the table is subject to re-adjustment.

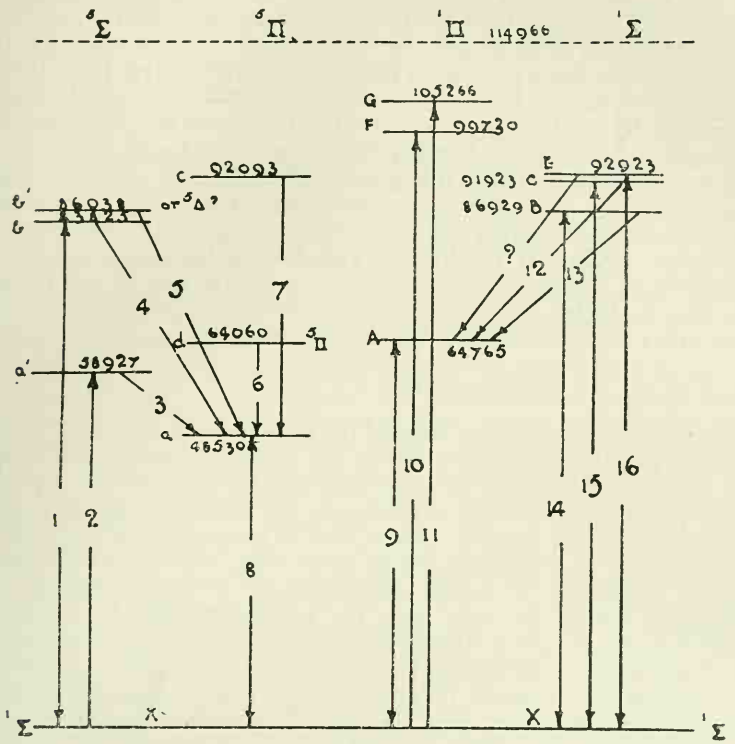


FIG. 3.

KEY TO FIG. 3.

No.	Description.	Reference.
(1)	Hopfield-Birge.	*Physical Rev.*, **29**, 922 (1927).
(2)	,,	,,
(3)	Asundi (new bands).	*Roy. Soc. Proc.*, **124**, 277 (1929).
(4)	Third Positive Carbon.	,,
(5)	"5*B*" bands (Wolters "spurious").	,,
(6)	Merton-Johnson "Triplet" bands.	,,
(7)	"3*A*" bands Duffendack-Fox.	,,
(8)	Cameron bands.	,,
(9)	Fourth Positive Carbon.	*Physical Rev.*, **28**, 1157 (1926).
(10)	Hopfield-Birge.	*Ibid.*, **29**, 922 (1927).
(11)	,,	,,
(12)	Herzberg-Johnson-Asundi.	*Roy. Soc. Proc.*, **123**, 560 (1929). *Z. Physik*, **52**, 815 (1929).
(13)	Ångström bands.	*Roy. Soc. Proc.*, **123**, 560 (1929).
(14)	Hopfield-Birge.	*Physical Rev.*, **29**, 922 (1927).
(15)	,,	,,
(16)	,,	,,

The Third Positive Carbon Bands.

The description of many of the levels given in Fig. 3 is a departure from the hitherto accepted views, and is based on an important recent paper by Asundi. In this paper a fine structure analysis of the (0, 0)

and (0, 1) bands of the third positive carbon system has been made, and it has been demonstrated that each band contains five P, five Q, and five R branches. This, together with other evidence, establishes the final level of this system as $^5\Pi$—incidentally, the first recorded case of a quintet level in band spectra. A suggestion of the present writer made some three years previously (*Nature*, Vol. 117, p. 376, 1926) is thus definitely confirmed. Prior to the work of Asundi, this level had been regarded as $^3\Pi$, and the gross structure of the bands was interpreted as due to three P and three Q heads, one of the latter being supposed too faint for observation, (*vide*, Birge, *Phys. Rev.*, Vol. 28, p. 1174, 1926). It would appear that this view must now be abandoned. Asundi's conclusion is that the Third Positive Carbon system (No. 4 in the diagram) arises from a $^5\Sigma \rightarrow {}^5\Pi$ transition. This has an important bearing on the scheme of electronic levels of the CO molecule, and as will be seen from Fig. 3, singlet and quintet terms appear adequate to explain the whole data: triplet levels are significantly absent, or at least unknown.

Nature of the Ground State of CO.

We shall consider further some of the consequences of Asundi's work. Although their fine structure analysis has not been done, it seems probable that there is a considerable resemblance between the Cameron bands and the third positive system, and the question arises as to what is the nature of the normal level of the CO molecule—the end state of this transition. On the generally-accepted view, it is a $^1\Sigma$ level, but the possible alternative $^5\Sigma$ merits consideration. In the latter case, the Cameron bands would arise from the transition $^5\Pi \rightarrow {}^5\Sigma$, while the fourth positive bands would be $^1\Pi \rightarrow {}^5\Sigma$, and both these transitions would account for the observed gross structure *if Hund's selection rule* $\Delta i_s = 0$ *is strictly preserved* (as is usually the case). Against this interpretation there is the fact that inter-system combinations (*i.e.*, $\Delta s \neq 0$) are not very probable, and we should certainly anticipate, on the above view, that the Cameron bands would be strong and the fourth positive bands weak in absorption. The reverse is actually the case, and this would be expected if the Cameron transition is $^5\Pi \rightarrow {}^1\Sigma$, and the fourth positive transition is $^1\Pi \rightarrow {}^1\Sigma$ (in emission). The most stable detailed configuration also points to $^1\Sigma$, and on the whole, it would seem better, pending further investigation, to accept the view that the normal state is $^1\Sigma$, recognising, of course, that the selection rule $\Delta i_s = 0$ is not here retained. It may be remarked in passing that the atmospheric O_2 absorption bands have been recently interpreted by Mulliken [4] as a transition $^1\Sigma \rightarrow {}^3\Sigma$, in which also the above selection rule is suspended. It would also, of course, be inevitable on the old view of the Cameron bands ($^3\Pi \rightarrow {}^1\Sigma$).[5]

Is the above $^5\Pi$ *Level Metastable?*

It is suggested that the above $^5\Pi$ level—which is the initial state of the Cameron bands—may be metastable. Alternatively, it may be some electronic level lower than a, and not yet discovered, which is metastable. We have the following facts: (1) At least 5 systems are known which have this level as their end state. Two or three of these are comparatively strong under ordinary conditions of excitation while the Cameron

[4] *Physical Rev.*, **32**, 880, 1928. [5] *Ibid.*, **32**, 396, 1928.

bands which represent the only way of transition to the normal state are, under these conditions, absent. (2) The Cameron bands are emitted under the exceptional conditions when CO molecules are present with an excess of Neon atoms. It would seem that in some way depending on the mechanism of collision, this metastability is destroyed and a transition to the ground state is effected.

Other Quintet Systems.

In the paper to which reference has already been made, some interesting conclusions are presented with regard to other CO band systems. The "$3A$" bands of Duffendack and Fox, when photographed under high dispersion were found to be 5-headed, with an over-all separation of $70 \cdot \nu$ for the (0, 0) band. Now, the over-all separation of the third positive bands is about $102{\cdot}5\ \nu$. These facts are satisfactorily explained by a ${}^5\Pi \rightarrow {}^5\Pi$ transition, the upper level having an extreme interval of about $32{\cdot}5\ \nu$ (*vide*, No. 7, Fig. 3).

System 5 of Fig. 3 constitutes a single n'' progression which has been regarded by some workers as the $n' = 1$ progression of the third positive carbon system. Its gross structure appears to be very confused, but it is probably 5-headed, and the separations, as far as can be judged, are of the same order as the latter system. The suggestion is therefore made that these bands constitute a separate system (designated "$5B$"), which possibly be from a ${}^5\Sigma$ or ${}^5\Delta$ level to ${}^5\Pi$.

A new band system (No. 3) is further announced by Asundi. Up to the present, this has been measured under low dispersion only. It extends from the green part of the spectrum into the infra-red, and is mingled with, and was at first thought to be a part of, the hitherto unassigned "triplet" bands of Merton and Johnson.[6] Unlike the latter bands, these appear best under normal conditions of excitation (*i.e.*, in the absence of Helium), and they constitute a new transition between a level hitherto recognised by Hopfield and Birge only in absorption, and the ${}^5\Pi$ level which is the final state of so many systems. The nature of the initial level is unknown (it is possibly ${}^5\Sigma$), but further information is promised.

Very little has been known hitherto about the so-called "triplet" carbon bands mentioned above. As their name suggests, each band under low dispersion appears to have three prominent heads. At the time of their discovery, a less conspicuous fourth head was recorded for most of the strong bands, and recent plates suggest that probably 5 heads are present. Work is at present in progress on this system by Mr. Asundi and myself: the details of this we hope to publish later. We have been able definitely to identify the final state of this system with the ${}^5\Pi$ level already discussed (*vide* No. 6, Fig. 3). This links the spectrum to the CO molecule and gives it a place in the electronic scheme. Its origin in CO has been suspected for some time. Mulliken, for example, suggested [7] that the system might possibly be a ${}^3\Pi \rightarrow {}^3\Sigma$ or ${}^3\Sigma \rightarrow {}^3\Pi$ transition in this molecule. With the final state of the system definitely identified as ${}^5\Pi$, the initial level is calculated to be approximately at $64060 \cdot \nu$, but this is necessarily subject to a reduction should further bands be found in the near infra-red. The over-all separation of the triplet bands near the origin is about $160 \cdot \nu$, as compared with about $102 \cdot \nu$ for the third positive bands. We may therefore deduce that the

[6] *Roy. Soc. Proc.*, A. **103**, 383, 1923. [7] *Physical Rev.*, **32**, 769, 1928.

initial level of the system is an inverted $^5\Pi$ with a separation of about 55-60 . ν, or alternatively, that if it is a *normal* $^5\Pi$ level, then the final $^5\Pi$ level is inverted. Considerations based on the detailed configurations of such states and their relative strengths, have led us to prefer the latter alternative. It has been represented in this way in Fig. 3 (No. 6). We are hoping that fine structure analysis may be possible in the case of some of the strongest bands of this system.

With regard to the singlet systems, it is scarcely necessary to make any comment here. The writer's views on Nos. 13 and 14 have been recently presented in co-operation with Mr. Asundi elsewhere.[8]

Structure of the CO Molecule.

The interpretation of the electronic states of the CO molecule, in terms of the detailed electronic configuration, was begun by Hund, and considerably extended by Mulliken, who has given details in recent papers.[9] The recognition of the quintet states already mentioned requires a new series of molecular configurations, and the whole of the levels will therefore be discussed in some detail. A comparison of the writer's conclusions with those of Mulliken is given in Table V. As a basis for discussion, the whole of the molecular states derivable from the ^3P, ^1D, and ^1S states of the oxygen and carbon atoms are collected in Table IV. The identification of the observed electronic states of CO with the appropriate states of Table IV. has been made. These data are given in

TABLE IV.

MOLECULAR STATES OF CO.

Atomic States.		Molecular States.	Configuration Summary.	Atomic States.		Molecular States.	Configuration Summary.
Fieldless.	With Field.			Fieldless.	With Field.		
C. O.	C. O.			C. O.	C. O.		
$^3P+{}^3P$	$^3\Sigma+{}^3\Sigma$	$2(^1\Sigma,{}^3\Sigma,{}^5\Sigma)$	$\sigma^{10}\pi^4$	$^1D+{}^1D$	$^1\Sigma+{}^1\Sigma$	$^1\Sigma,{}^1\Sigma$	$\sigma^{12}\pi^2$
	$^3\Sigma+{}^3\Pi$	$^1\Pi,{}^3\Pi,{}^5\Pi$	$\sigma^9\pi^5$		$^1\Sigma+{}^1\Pi$	$^1\Pi$	$\sigma^{11}\pi^3$
	$^3\Pi+{}^3\Sigma$	$^1\Pi,{}^3\Pi,{}^5\Pi$	$\sigma^{11}\pi^3$		$^1\Sigma+{}^1\Delta$	$^1\Delta$	$\sigma^{12}\pi^2$
	$^3\Pi+{}^3\Pi$	$^{1,3,5}\Sigma,{}^{1,3,5}\Delta$	$\sigma^{10}\pi^4$		$^1\Pi+{}^1\Sigma$	$^1\Pi$	$\sigma^{11}\pi^3$
$^1D+{}^3P$	$^1\Sigma+{}^3\Sigma$	$^3\Sigma$	$\sigma^{12}\pi^2$		$^1\Pi+{}^1\Pi$	$^1\Sigma,{}^1\Delta$	$\sigma^{10}\pi^4$
	$^1\Pi+{}^3\Sigma$	$^3\Pi$	$\sigma^{11}\pi^3$		$^1\Pi+{}^1\Delta$	$^1\Pi,{}^1\Phi$	$\sigma^{11}\pi^3$
	$^1\Delta+{}^3\Sigma$	$^3\Delta$	$\sigma^{10}\pi^4$		$^1\Delta+{}^1\Sigma$	$^1\Delta$	$\sigma^{10}\pi^4$
	$^1\Sigma+{}^3\Pi$	$^3\Sigma$	$\sigma^{11}\pi^3$		$^1\Delta+{}^1\Pi$	$^1\Pi,{}^1\Phi$	$\sigma^9\pi^5$
	$^1\Pi+{}^3\Pi$	$^3\Sigma,{}^3\Delta$	$\sigma^{10}\pi^4$		$^1\Delta+{}^1\Delta$	$^1\Sigma,{}^1\Gamma$	$\sigma^{10}\pi^4$
	$^1\Delta+{}^3\Pi$	$^3\Pi,{}^3\Phi$	$\sigma^9\pi^5$	$^1S+{}^1D$	$^1\Sigma+{}^1\Sigma$	$^1\Sigma,{}^1\Sigma$	$\sigma^{10}\pi^4$
$^1S+{}^3P$	$^1\Sigma+{}^3\Sigma$	$^3\Sigma$	$\sigma^{10}\pi^4$		$^1\Sigma+{}^1\Pi$	$^1\Pi$	$\sigma^9\pi^5$
	$^1\Sigma+{}^3\Pi$	$^3\Pi$	$\sigma^9\pi^5$		$^1\Sigma+{}^1\Delta$	$^1\Delta$	$\sigma^{10}\pi^4$
$^3P+{}^1D$	$^3\Sigma+{}^1\Sigma$	$^3\Sigma$	$\sigma^{10}\pi^4$	$^3P+{}^1S$	$^3\Sigma+{}^1\Sigma$	$^3\Sigma$	$\sigma^8\pi^6$
	$^3\Sigma+{}^1\Pi$	$^3\Pi$	$\sigma^9\pi^5$		$^3\Pi+{}^1\Sigma$	$^3\Pi$	$\sigma^9\pi^5$
	$^3\Sigma+{}^1\Delta$	$^3\Delta$	$\sigma^{10}\pi^4$	$^1D+{}^1S$	$^1\Sigma+{}^1\Sigma$	$^1\Sigma,{}^1\Sigma$	$\sigma^{10}\pi^4$
	$^3\Pi+{}^1\Sigma$	$^3\Pi$	$\sigma^{11}\pi^3$		$^1\Pi+{}^1\Sigma$	$^1\Pi$	$\sigma^9\pi^5$
	$^3\Pi+{}^1\Pi$	$^3\Sigma,{}^3\Delta$	$\sigma^{10}\pi^4$		$^1\Delta+{}^1\Sigma$	$^1\Delta$	$\sigma^8\pi^6$
	$^3\Pi+{}^1\Delta$	$^3\Pi,{}^3\Phi$	$\sigma^{11}\pi^3$	$^1S+{}^1S$	$^1\Sigma+{}^1\Sigma$	$^1\Sigma,{}^1\Sigma$	$\sigma^8\pi^6$

Columns 1-5 of Table V. In Column 7 are given the probable dissociation products for each electronic state. The complete specification for each

[8] *Roy. Soc. Proc.*, A. **123**, 560, 1929.
[9] *Physical Rev.*, **32**, 206; and 768, 1928.

TABLE V.

Configurations of the CO Molecule.

Level.	ν_e (Approx.)	ω_0 (Approx.).	Type.	Configuration.	(Johnson.)								Dissociation Products.		Type (Old View).	(Mulliken.)					
					$2p\pi$	$3s\sigma$	$3p\sigma$	$3p\pi$	$3d\sigma$	$3d\pi$	$4s\sigma$	$4p\sigma$	C.	O.		$2p\pi$	$3s\sigma$	$3p\sigma$	$3p\pi$	$3d\sigma$	$3d\pi$
X	0	2155	$^1\Sigma$	$\sigma^{10}\pi^4$	4	2	2	—	—	—	—	—	$^3P(\sigma^4\pi^2)$	$^3P_i(\sigma^6\pi^2)$	$^1\Sigma$	4	2	2	—	—	—
a	48,530	1726	$^5\Pi_i$	$\sigma^9\pi^5$	3	1	2	2	—	—	—	—	$^3P(\sigma^4\pi^2)$	$^3P_i(\sigma^5\pi^3)$	$^3\Pi$	4	1	2	1	—	—
a'	58,927	1155	$^5\Sigma$?	$\sigma^{10}\pi^4$	2	2	2	2	—	—	—	—	$^3P(\sigma^4\pi^2)$	$^3P_i(\sigma^6\pi^2)$	$^3\Sigma$?	3	2	2	1	—	—
d	64,060	1105	$^5\Pi$	$\sigma^{11}\pi^3$	2	2	2	1	1	—	—	—	$^3P(\sigma^5\pi)$	$^3P_i(\sigma^6\pi^2)$	?						
b	83,825	?	$^5\Sigma$	$\sigma^{10}\pi^4$	3	1	2	1	1	—	—	—	$^3P(\sigma^5\pi)$	$^3P_i(\sigma^5\pi^3)$	$^3\Sigma$	4	1	2	—	1	—
b'	86,038	?	$^5\Delta$?	$\sigma^{10}\pi^4$	3	1	2	1	—	1	—	—	$^3P(\sigma^5\pi)$	$^3P_i(\sigma^5\pi^3)$	?						
c	92,093	?	$^5\Pi_i$	$\sigma^9\pi^5$	3	—	2	2	—	—	—	1	*$^3P(\sigma^4\pi^2)$	$^3P_i(\sigma^5\pi^3)$	$^3\Sigma$	4	2	1	1	—	—
A	64,765	1502	$^1\Pi$	$\sigma^9\pi^5$	4	1	2	1	—	—	—	—	$^3P(\sigma^4\pi^2)$	$^3P_i(\sigma^5\pi^3)$	$^1\Pi$	4	1	2	1	—	—
B	86,929	2132	$^1\Sigma$	$\sigma^{10}\pi^4$	4	1	2	—	—	—	1	—	$^1D(\sigma^5\pi)$	$^1D(\sigma^5\pi^3)$	$^1\Sigma$	4	1	2	—	1	—
C	91,923	?	$^1\Sigma$	$\sigma^{10}\pi^4$	4	1	2	—	—	—	—	1	$^1D(\sigma^4\pi^2)$	$^1D(\sigma^6\pi^2)$	$^1\Sigma$?						
E	92,923	(2134)	$^1\Sigma$?	$\sigma^{10}\pi^4$	3	2	2	—	—	1	—	—	$^1S(\sigma^4\pi^2)$	$^1D(\sigma^6\pi^2)$	$^1\Sigma$	3	2	2	—	—	1
F	99,730	1916	$^1\Pi$?	$\sigma^{11}\pi^3$	3	2	2	—	1	—	—	—	$^1D(\sigma^5\pi)$	$^1D(\sigma^6\pi^2)$	$^1\Pi$?	3	2	2	—	1	—
G	105,266	?	?	?											?						

Notes.—(1) * One of these ^3P atoms (possible the C atom), is in an excited state, 3^3P. One of the atoms is necessarily excited, since the term ν . 92,093 exceeds the value of D (= 11·2 volts = ν . 90,720). Moreover, only a combination of two ^3P atoms will give a $^5\Pi$ state.

(2) The suggested dissociation products of states C, E, F, are tentative only, and in the absence of Heat of Dissociation data will remain uncertain.

(3) The value of D derived from the B state, which is between 2 and 3 volts above the normal, indicates two excited atoms, if correct. Unfortunately, the ^1D state of the oxygen atom is metastable, and the value of ^3P—^1D is unknown. In the absence of this knowledge the dissociation products suggested for the B state are necessarily tentative.

(4) In the detailed configurations the six electrons $(1s\sigma)^2(2p\sigma)^2(2s\sigma)^2$ are common to all states, and have been omitted.

electron orbit is in Column 6. In preparing this, the allocation is such as to give (in conformity with Table I.) the correct molecular state. A number of alternative allocations, all of which give the correct state, usually appear at this stage, and in selecting the right one, the following considerations are weighed : (1) the relative strengths of binding of the molecule in the various states—as evidenced by ω_0, r_0, or D^v; and (2) the various electronic transitions which are known to occur, and the relative probability of them. It is obvious that when allocations have been made which give the molecular states and appear to satisfy condition (1), they must also, as a rule, account for the strong band systems by a *single* electronic transition for which also $\Delta l_\tau = \pm 1$. (While $\Delta l = 0$ is not impossible, it is generally less favoured in light molecules. The whole question is very difficult, however, depending on the precise interpretation of l in terms of the molecular model, and no very definite rules can be laid down.[10] Further, it will be apparent that a system requiring simultaneous transitions of two electrons, will be considerably less favoured than one which requires a change of only one electron.

For purposes of comparison, the hitherto accepted views of the electronic levels, together with Mulliken's interpretation of them, are embodied in Table V. We shall proceed to consider some of the details of this table. Level *d*, the initial level of the triplet carbon bands of Merton and Johnson has some seven known vibrational levels associated with it, and from these I have determined the value of D as 11·8 volts. This is probably fairly reliable, and definitely indicates that the dissociation products are two normal atoms. Of the two $^5\Pi$ levels *d* and *a*, the configuration $A(2p\pi)^3(3s\sigma)(3p\sigma)^2(3p\pi)^2$ is considered to involve a closer binding than $A(2p\pi)^2)3s\sigma)^2(3p\sigma)^2(3p\pi)(3d\sigma)$, and hence these were associated respectively with the final and initial levels for which $\omega_0 = 1726$ and 1105. The level *a* is therefore the inverted $^5\Pi_i$ level, while *d* is normal. It follows that the configuration change giving the triplet carbon bands ($\sigma^{11}\pi^3 \rightarrow \sigma^9\pi^5$) must involve simultaneous change in two electrons, *viz.*, $3d\sigma \rightarrow 3p\pi$ and $3s\sigma \rightarrow 2p\pi$. It would seem that the conditions under which this is possible are provided by the high-pressure helium or argon necessary for the strong development of this spectrum. The single transition $3d\sigma \rightarrow 3p\pi$ should presumably occur, but the resulting band system would be in the infra-red at about 2μ.

The two most probable $^5\Sigma$ configurations appear to be those given to the levels *a'* and *b*. Level *a'* represents a considerably looser binding than *a* (as estimated by ω). The ω_0 for *b* is not known, as the progression formerly interpreted as $n' = 1$ is now suggested to be a new level *b'*. The inter-nuclear distance in state *b* is, however, smaller than *a*, *viz.*, 1·10 Å.U., as compared with 1·24 Å.U., thus indicating a closer binding. The assignment of the two configurations has been made correctly as between *a'* and *b*, but the configuration assigned to *b* appears doubtful when the binding of states *b* and *a* are compared. We may, of course, postulate—in the absence of evidence to the contrary—that a possible distinction is to be drawn here between the evidence of distance bonding power and that (unknown) of energy bonding power. An alternative configuration might, however, be considered for state *b*, *viz.*,

$$A(2p\pi)^3(3s\sigma)^2(3p\sigma)(3p\pi)(3d\sigma).$$

This gives a $^5\Sigma$ level with possibly closer binding than *a*, but it requires the overwhelming disadvantage of requiring a 2-electron transition to

[10] *Vide* Mulliken, *loc. cit.*, pp. 194 and 220.

give the strong third positive carbon system, and also a 2-electron transition (one involving $\Delta l = 0$) to reach the ground state (No. 1, Fig. 3). The configuration of Table V. gives the third positive system by the single favoured transition $3d\sigma \rightarrow 3p\pi$, and the Hopfield-Birge system No. 1 by the favourable 2-electron transitions $3d\sigma \rightarrow 2p\pi$ and $3p\pi \rightarrow 3s\sigma$. We have, therefore, little doubt in retaining the configuration as given in Table V.

With regard to level *a*, evidence has already been given that it may be metastable. It is of interest to examine the $a \rightarrow X$ transition responsible for the Cameron bands. A 2-electron transition is necessary, $3p\pi \rightarrow 3s\sigma$ and $3p\pi \rightarrow 2p\pi$. We may, therefore, interpret the metastability of this level as due to the unfavourable character of the latter transition $3p\pi \rightarrow 2p\pi$. If, however, it is possible to effect a breakdown of the coupling of the two $3p\pi$ electrons without the dual transition being inevitable, it seems possible that a stable electronic state may exist lower than *a*, having the configuration $A(2p\pi)^3(3s\sigma)^2(3p\sigma)^2(3p\pi)$. Theoretically it might be $^3\Delta_i$, $^3\Sigma$, $^1\Delta$ or $^1\Sigma$, but $^3\Sigma$ is suggested as not unlikely. If such a hypothetical state exists, it will probably have an ω_0 of about 2000 (or more), and the metastability would be associated with it rather than with *a*.

With regard to the state *b'*, very little is known, and there is no object in discussing it. The configuration given to the state *c* gives a plausible transition $4p\sigma \rightarrow 3s\sigma$ to the "$3A$" bands, and, moreover, makes fairly probable an excited *P* atom as one of the dissociation products. The necessity for this is mentioned in a footnote to Table V.

Turning to the singlet states, there can be little doubt about A. The configuration of B is slightly different to Mulliken's. The outermost electron is believed to be in a $4s\sigma$ rather than a $3d\sigma$ orbit, and for three reasons: (1) The transition to the ground state (No. 14, Fig. 3) can be effected more favourably: $4s\sigma$ to $3s\sigma$ is less unfavourable than $3d\sigma \rightarrow 3s\sigma$; (2) It is believed to be more consistent with the dissociation products, which are thought to be two excited atoms; (3) The "effective" quantum numbers for the electrons in the X ($^1\Sigma$) level and the B ($^1\Sigma$) level are calculated by Birge as ·9767 and 1·9778 respectively, so that the two terms must be members of the same series. The orbits of the electron are therefore interpreted as $3s\sigma$ and $4s\sigma$ respectively. A certain element of doubt exists as to the dissociation products of state *B*. This, we have mentioned as a footnote to the table.

An element of uncertainty also exists as to the configuration assigned to state *C*. The exceptional closeness of the distance bonding power to that of state B[11] makes it inevitable that the internal configurations should be similar. With the outer electron in a $4p\sigma$ orbit, the transition to $3p\pi$ is associated with $\Delta l = 0$, while that to the normal state $4p\sigma \rightarrow 3s\sigma$ is favoured. On the other hand, $3d\sigma$ as an alternative to $4p\sigma$ is favourable as regards the transition to $3p\pi$ (the A level), but very unfavourable, if not impossible, as regards the transition to X which would involve $\Delta l = 2$.

If state E is $^1\Sigma$, its structure is probably as given by Mulliken, having the outermost electron in a $3d\pi$ orbit. The transition to the normal state (a $2p\pi$ orbit) is then favourable. An $E \rightarrow A$ system would involve the two-electron transition $3d\pi \rightarrow 2p\pi$ and $3s\sigma \rightarrow 2p\pi$, so that such a transition would be comparatively faint. Any evidence for it is at

[11] *Vide Roy. Soc. Proc.*, A. **123**, 569, 1929; $r_0 = 1{\cdot}1228$ and $1{\cdot}1220$ Å.U. respectively.

present doubtful.[12] There is one point which does not seem quite in harmony with the above configuration: the value of ω_0, as given by Birge, is of the order 2134. If this is substantiated, it would seem to be rather large for the proposed configuration.

Comparatively little is known of the F level, which appears only as the upper state of one of the Hopfield-Birge absorption systems. It is satisfactorily accounted for by the configuration given by Mulliken. As with the E level, any transition such as $F \rightarrow A$ or $F \rightarrow B$ would involve a 2-electron transition and the corresponding band spectra would be faint.

[12] *Vide Roy. Soc. Proc.*, A. **123**, 573, 1929.

THE ELECTRONIC STRUCTURE OF SOME DIATOMIC MOLECULES.

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I.

A knowledge of the electronic structure of molecules is of the greatest importance, both to the physicist and the chemist; to the physicist because the facts of molecular spectra can only be interpreted in terms of electronic structure, to the chemist because a detailed knowledge of electronic structure is necessary to indicate the exact conditions (of excitation, etc.), under which atoms will combine to form molecules. A number of methods, both experimental and theoretical, have recently been converging to a solution of this problem. On the experimental side there is the important work of Franck[1] and his collaborators, who have shown how a molecule splits up by light absorption into its component atoms (or ions). This work shows that in most cases a normal molecule splits up (adiabatically) into two unexcited atoms or ions. This work must now be supplemented by the important results of Herzberg,[2] who has shown that in some cases a molecule in its normal state splits up into one normal and one excited component. In these cases it is an excited molecule which leads on dissociation to two normal components. The converse must be true, so that, for example, an *excited* C atom and a *normal* N atom are necessary to produce a *normal* CN molecule.

The recent advances on the theoretical side are the direct outcome of the new quantum mechanics, as the older theory was incapable of dealing with the simplest molecules. The first new and important concept was Heisenberg's idea of resonance in atoms.[3] This led, as is well known, to a satisfying explanation of the ortho- and para-system of helium, and to a general explanation of multiplet spectra. Of the possible spectral terms, which can arise from a given outer group of electrons, the one of

[1] Franck, *Trans. Farad. Soc.*, **21**, 536 (1925); Franck, Kuhn, and Rollefson, *Z. Physik*, **43**, 155 (1927); H. Sponer, *Ergebnisse d. exakt. Naturwissen.*, **6**, 75 (1927).

[2] Herzberg, *Ann. Physik*, **86**, 189 (1928); Heitler and Herzberg, *Z. Physik*, **53**, 52 (1929).

[3] Heisenberg, *Z. Physik*, **38**, 411; **39**, 499 (1926); **41**, 239 (1927).

greatest multiplicity has the lowest energy and of the terms with the same multiplicity the one with the greatest "l" value is lowest. The same result is doubtless true also of molecular terms.

The natural extension of the resonance principle of Heisenberg to an "*Austausch*" principle was made by Heitler and London.[4] Although the underlying ideas are somewhat different, the mathematical analysis is practically identical. It was shown that the exchange between the electrons of two hydrogen atoms led to an energy lower than that of the separated atoms; in other words, it led to the formation of a molecule. This important result has since been extended by Heitler and London.[5] The latter has shown that the new theory gives a quantum mechanical explanation of the empirical ideas of Lewis and others concerning chemical valency and correlates the idea of valency with that of electron spin. Although the general conditions under which binding can occur in a quantum mechanical sense, have now been well developed, only one case has been worked out quantitatively, *viz.*, that of the hydrogen molecule. Certain difficulties have appeared in more complicated cases, as, for instance, in O_2 and F_2, where the theory is unable to account for molecular binding, and at the same time to account for the $^3\Sigma$ ground level of O_2. We shall refer to this point later and shall suggest a possible explanation. Of the possible molecular states which can arise from atoms in given atomic states, the theory as developed at present indicates that the one of lowest multiplicity has the lowest energy, though this is not always true (as in O_2, for example). The theory is not yet able to say what is the relative energy of terms of *like* multiplicity.

An exhaustive treatment of the relation between atomic spectral terms and the molecular terms which are possible on bringing two atoms together has been made by Wigner and Witmer.[6] This theory gives *all* the molecular terms which are theoretically possible to satisfy the requirements of group theory, but it gives no indication which of the possible terms correspond to stable molecular states and which to unstable. Thus, two F atoms in ^2P states could give rise to one Δ molecular state, two Π states and three Σ states, and each could be a singlet or a triplet. The theory gives no idea which of them actually occur or what is the relative depth of the energy levels.

The most important work on the problem of the detailed electronic structure of molecules has been done by Hund [7] and Mulliken,[8] who have ascribed to each electron in a molecule a definite and unique quantum notation. In the first place, each electron is regarded as having a definite quantised angular momentum about the molecular axis. When this is zero, the electron is described as a σ electron; similarly, when it has the values, 1, 2, . . . , it is said to be a π, δ, . . . electron, in analogy with the s, p, d, . . . notation in atoms. In the second place, the electron is given those *atomic* quantum numbers which it would have, if the atoms of the molecule were pushed together to form one united atom. This defines each electron uniquely. Thus, we may have $2s\sigma$, $2p\sigma$, $2p\pi$, . . . electrons. The Pauli Principle is assumed to hold in molecules as in atoms, so that it is assumed that there are not more than two electrons

[4] Heitler and London, *Z. Physik*, **44**, 455 (1927).
[5] Heitler, *Z. Physik*, **46**, 47, **47**, 835, **51**, 805 (1928); London, *Z. Physik*, **46**, 455, **50**, 24 (1928).
[6] Wigner and Witmer, *Z. Physik*, **51**, 859 (1928).
[7] Hund, *Z. Physik*, **51**, 759 (1928).
[8] Mulliken, *Physical Rev.*, **32**, 186 (1928).

in the same σ-state, but as a π-electron may have an angular momentum of $+1$ or -1, there can be four, and not more than four, electrons in the same π-state. The electronic structure of a molecule may then be given unambiguously, as, for example, $1s\sigma^2$, $2p\sigma^2$, $2s\sigma^2$, $2p\pi^3$, $3p\sigma$, the upper index indicating in each case the number of "equivalent" electrons.

The next problem considered by Hund [7] is the relative energies of these various electron levels. This is known, of course, in the limiting case when the internuclear distance is zero and molecular states become atomic states. Thus, we have the series $1s^2$, $2s^2$, $2p^6$, $3s^2$, . . . When the nuclei are pulled slightly apart, Hund gives reasons for supposing that the series of corresponding molecular states is $1s\sigma^2$, $2s\sigma^2$, $2p\sigma^2$, $2p\pi^4$, $3s\sigma^2$, . . . Again, the energy levels of another limiting case is known, *viz.*, that in which the component atoms are infinitely distant. By considering the splitting of the degenerate states which the work of Heitler and London indicates, another series of energy levels can be written down. For the intermediate stages which actual molecules occupy, a series of energy levels is assumed by interpolation, and is adjusted so as to fit in with many known facts and to give a smooth transition from the one extreme limiting case to the other.

The character of a molecular term is determined in the first place by the resultant angular momentum of all the electrons about the nuclear axis. When this is zero, the term is described as a Σ term; similarly, when it is one, two, . . . , the terms are denoted by Π, Δ, . . ., in analogy with the S, P, D, . . . notation of atoms. The multiplicity is denoted as usual by an index on the left-hand side, as in $^2\Pi$, $^3\Sigma$, and so on. A closed molecular group, whether σ or π, must give a $^1\Sigma$ term, as the resultant angular momentum and the resultant electron must both be zero.

Both Hund and Mulliken have found it necessary to supplement the table of energy levels by certain empirical rules. The former uses a working hypothesis to limit the intersections of the possible transitions from a given state of the separated atoms to the corresponding states of the united atom. The latter uses the hypothesis that the number of σ, π, . . . electrons remains constant during possible transitions. Both methods have met with considerable success, and have led to a better understanding of the structure of the more complicated diatomic molecules, like N_2. Further, they have obtained analogous electronic structures for certain series of diatomic molecules with a like number of electrons and are thus able to explain why these molecules should have similar physical properties, a well-known but otherwise unexplained fact.

There are, however, certain difficulties in the theories of Hund and Mulliken, as has been pointed out by Herzberg.[9] In particular, they are not capable of explaining the experimental results obtained by Herzberg,[10] and interpreted by Heitler and Herzberg,[11] *viz.*, that N_2^+ in the normal state, splits up into a normal N atom and an excited N ion. Similar results hold also in the cases of CN, CO^+, BO and SiN. Herzberg [9] has proposed a modification of the Hund-Mulliken scheme to bring it more in line with the Heitler and London ideas, and has used as a working hypothesis that each electron in the transition from atom to molecule

[9] *Z. Physik*, to appear shortly. I am greatly obliged to Dr. Herzberg for letting me see an advance copy of his paper and for many interesting discussions of the points at issue.

[10] Herzberg, *Ann. Physik*, **86**, 189, 1928.

[11] Heitler and Herzberg, *Z. Physik*, **53**, 52, 1929.

retains its own characteristic quantum numbers (in the Hund-Mulliken notation).

It seems to the writer that there is a great disadvantage in relating the notation of electrons in molecules to a condition which cannot be realised. It is more important to know what happens to a molecule on dissociation than to know what happens when it is compressed to form a single atom. Further, the Hund-Mulliken notation would become somewhat complicated if extended to heavy atoms for there is a progressive increase in the quantum numbers required. Even for atoms with principal quantum number 2, it is necessary to use the symbols $3d\pi$ and $4p\sigma$ for the molecular states, and such states are not readily interpreted. Further, the notation gives no indication as to whether the various electronic states in a molecule correspond to binding or repulsion. These difficulties are due to the attempt to preserve the Pauli Principle in molecules so as to have not more than two electrons with given quantum numbers. There are thus only two electrons in each molecule with principal quantum 1. There must, however, be a limit for practical purposes to such an application of the Pauli Principle, otherwise it would be necessary to give a different notation for every pair of K electrons in a solid (say, a lump of lead). It seems more reasonable and practicable in heavy molecules to allot two K electrons to *each* nucleus. We shall regard the Pauli Principle as fulfilled when we say that two K electrons "belong" to a nucleus A and two to a nucleus B. Similarly, there must be a stage when it is more convenient to assign a complete group of L electrons to each nucleus. A distinction is therefore drawn in this paper between *atomic* levels and *molecular* levels, even in a molecule. The latter are those which arise from an "*Austausch*" phenomenon in the Heitler and London sense, and give binding. There is also a set of levels, which give rise to repulsion, the corresponding *eigenfunctions* having a certain *asymmetry* not possessed by the "binding" or "molecular" levels. The main purpose of this paper is to show that these levels should not be considered in the process of building molecules in their normal states.

An "*Aufbau*" Principle is adopted which assigns the electrons one by one to a molecule, and places them in the lowest available molecular and atomic levels subject to certain rules which have to be observed in order not to conflict with the Heitler-London requirements.

The assigning of electrons to molecular levels leads to the idea of *resonance between molecular states* when two electrons are in different molecular levels. In such a case, that state is held to be lowest which has the greatest multiplicity, as is the case in atoms. Examples occur in Bo_2 and O_2, which should both be $^3\Sigma$ states in the normal level, and therefore paramagnetic, while the lowest state of N_2 is a $^1\Sigma$ state, and is therefore diamagnetic.

II.

In the older quantum theory, one was guided in the assignment of quantum numbers to electrons in atoms by the quantum numbers necessary to specify the different orbits in the simple hydrogen atom. Owing to the effect of the core, the energy levels of electrons in the outer shells were different from those of hydrogen, but nevertheless "effective" quantum numbers were deduced for the various levels, and it was in general easy to infer the correct "true" quantum numbers. Except in

the more complicated atoms, it was possible to use an Aufbau Principle, whereby the electrons were added one at a time to the nucleus, and were placed in the orbits corresponding to the progressive changes in the hydrogen quantum numbers. The Bohr (or, later, the Stoner) subgroups were successively filled by electrons. It was found permissible to assume as a first approximation that the energy of electrons in outer incomplete groups was not seriously modified by the other outer electrons, that is, electrons with the same n, but different l.

As a second approximation, it was possible to combine the "l" (or angular momentum) values of incompleted groups vectorially to give different effective or resultant L values. This resultant L determined the spectral type, which was denoted by S, P, D . . . according as it had the values 0, 1, 2, . . .

Next, the coupling between spin momenta of the electrons gave a "resultant" spin vector S, which determined the multiplicity. The multiplicity was given by $R = 2S + 1$, if S was measured in units of $h/2\pi$. Finally, the components of a multiplet were regarded as determined by the coupling between the resultant L vector and the resultant S vector.

These vectors methods have proved not to be of general applicability, but the results obtained thereby are in most cases confirmed by the more well-founded "resonance" methods of Heisenberg.[3] In particular, both lead to the same relative energy values of the various multiplet terms, which can arise from a given number of outer electrons with prescribed n and l values.

We seek a similar and analogous method for molecule-building. First we consider the possible energy levels of *one* electron in the presence of a two-nuclear system. An accurate analytical solution of the two-centre-problem is not yet possible, but certain approximate methods can now be used to indicate the relative position of the various energy levels—in each case as a function of internuclear distance. We use this system of energy levels for the many-electron problem just as was done in atoms. We then suppose a molecule built up in the following way. We add one charge at a time to each nucleus and then, supposing the nuclei held fixed, add to the system two electrons successively. The system is then allowed to take up its equilibrium value adiabatically.

Next, we add the components of the angular momenta about the nuclear axis. This determines the spectral type, Σ, Π, or Δ, etc. Then as in atoms, we add the electron spins to determine the multiplicity.

In most molecules, the electronic energy is much greater than that due to vibration and so, when the nuclei are no longer held fixed, a series of energy levels arise due to the same electron configuration but different quantised vibrations. We assume that the vibration does not seriously modify the electron configuration. Again, when rotation takes place, it may in general be assumed that neither the electronic configuration nor the vibration energy are greatly perturbed. This is not true of the light molecule He_2, where an uncoupling of the "l" values from the nuclear axis takes place when the rotation is large.[12] We shall not enter this problem, but shall mostly confine ourselves to ground levels or to excited states of the heavier molecules.

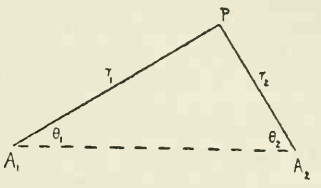
[12] Weizel, *Z. Physik*, **52**, 175 (1929); **56**, 727 (1929).

III.

The Schrödinger equation for an electron (of mass μ) under the influence of two nuclei of charges ze, is

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}\left(E + \frac{ze^2}{r_1} + \frac{ze^2}{r_2} + \Omega(R)\right)\psi = 0 \quad . \quad . \quad (1)$$

where R is the distance between the nuclei and $\Omega(R)$ is the potential of the forces which depend only on the internuclear distance. When $R \to \infty$, the equation tends, of course, to that of the hydrogen atom with nuclear charge ze at A_1, the solutions of which are known. For a total quantum n, there are n^2 solutions with the same energy E_n, of which $\psi_{n,l,m}$ is typical. Similarly, there are corresponding solutions $\chi_{n,l,m}$ with the same energy about the nucleus A_2; ψ and χ are functions of the co-ordinates r_1, θ_1, and ϕ, r_2, θ_2 and ϕ respectively, shown in the fiigure; ϕ is the azimuthal angle which determines the position of the plane PA_1A_2 about A_1A_2.



Using the Heitler and London [4] method, we find that the appropriate molecular *eigenfunctions* are

$$\Phi'_{n,l,m} = (\psi_{n,l,m} - \chi_{n,l,m})/\{2(1 - S_{n,l,m})\}^{\frac{1}{2}} \quad . \quad . \quad (2)$$

$$\Phi''_{n,l,m} = (\psi_{n,l,m} + \chi_{n,l,m})/\{2(1 + S_{n,l,m})\}^{\frac{1}{2}} \quad . \quad . \quad (3)$$

where

$$S_{n,l,m} = \int \psi_{n,l,m}\bar{\chi}_{n,l,m}d\tau,$$

an integral over the whole of space. These solutions are only approximations of zero order, and only valid for large values of R. Other methods must be used for small values of R. This we shall consider below.

The perturbed energies are easily worked out by the Heitler and London method. We find

$$E'_{n,l,m} = E_n + \epsilon'_{n,l,m} + \Omega(R)$$
$$E''_{n,l,m} = E_n + \epsilon''_{n,l,m} + \Omega(R)$$

where

$$\epsilon'_{n,l,m} = -ze^2(I_{n,l,m} - J_{n,l,m})/(1 - S_{n,l,m})$$
$$\epsilon''_{n,l,m} = -ze^2(I_{n,l,m} + J_{n,l,m})/(1 + S_{n,l,m})$$

and E_n has already been defined as the energy when the nuclei are infinitely distant and the electron belongs to one nucleus. The symbol $S_{n,l,m}$ has also been defined; $I_{n,l,m}$ and $J_{n,l,m}$ are similar integrals over the whole space given by

$$I_{n,l,m} = \int(\psi_{n,l,m}\bar{\psi}_{n,l,m}/r_2)d\tau$$
$$J_{n,l,m} = \int(\psi_{n,l,m}\bar{\chi}_{n,l,m}/r_1)d\tau.$$

These integrals for $n = 1$, $l = 0$, $m = 0$ have already been worked out by Pauling [13] and Morse and Stueckelberg.[14] The latter have also con-

[13] Pauling, *Chemical Reviews*, **5**, 173 (1928).
[14] Morse and Stueckelberg, *Physical Rev.*, **33**, 932 (1929).

sidered higher quantum numbers, but unfortunately their work is marred in the later stages by an error, which leads to wrong values of the integrals. They write the unperturbed *eigenfunctions* of the hydrogen atom in terms of parabolic co-ordinates, and then by a very neat method trace the change in the character of the nodes as two nuclei are brought together. They consider *eigenfunctions*, $\psi \pm \chi$, in parabolic co-ordinates, the plus sign giving a function which is symmetrical about the plane bisecting the nuclear axis at right angles, and the negative sign giving an unsymmetrical function. The latter, therefore, has an extra node consisting of the mid-plane. The parabolic co-ordinates are gradually changed to elliptic co-ordinates as the nuclei are brought together, with a consequent change in the nodes. Finally, when the nuclei are brought close together, the elliptic co-ordinates change to spherical polar co-ordinates. The nodes in this case give the corresponding *eigenfunction* in the united atoms. Morse and Stueckelberg then consider a perturbation of this *eigenfunction* for small values of the internuclear distance, and thus obtain information about the perturbation energy in a region where the Heitler and London method does not apply. We shall use their results in this connection later in this paper.

The authors then consider the perturbation energy for large internuclear distances, and do so by a transformation of the functions $\psi \pm \chi$ from parabolic to elliptic co-ordinates. Unfortunately, they use a transformation which is true only for infinitely large distances. Now, if the Heitler and London method is to be applicable, ψ and χ must both be *exact* solutions of the Schrödinger equation for hydrogen whatever co-ordinates are used. If, for instance, λ_1 and λ_2 are the parabolic co-ordinates of a specified point P, referred to A_1 as focus, then λ_1 and λ_2 must be transformed *exactly* to elliptic co-ordinates. This can be done as follows :—

$$\lambda_1 = r_1(1 + \cos\theta_1) = (R/2)(1 + \rho + \mu + \rho\mu),$$
$$\lambda_2 = r_2(1 - \cos\theta_2) = (R/2)(\rho + \mu - \rho\mu - 1),$$

where ρ and μ are elliptic co-ordinates, given by

$$\rho = (r_1 + r_2)/R, \quad \mu = (r_1 - r_2)/R.$$

Similarly, the parabolic co-ordinates λ_1', λ_2' of the *same* point P referred to a second point A_2 as focus, and the same axis A_1A_2 become

$$\lambda_1' = (R/2)(\rho - \mu + \rho\mu - 1),$$
$$\lambda_2' = (R/2)(\rho - \mu - \rho\mu + 1).$$

If the *eigenfunction* ψ is written as a function of λ_1 and λ_2, then χ must be written as the same function of λ_1' and λ_2', in order that $\psi + \chi$ may have the required symmetry in the mid-plane.

When these transformations are used, the results become the same as those obtained in this paper, except that the molecular *eigenfunctions* $\psi \pm \chi$ are linear expansions of the molecular *eigenfunctions* obtained here. This is to be expected, since the hydrogen *eigenfunctions* expressed in parabolic co-ordinates are only linear expansions of the usual hydrogen *eigenfunctions* in spherical polar co-ordinates.

In this paper we shall confine ourselves to states of total quantum number 2, which suffice to deal with the series of diatomic molecules Li_2 to F_2 and serve to bring out the main points of the paper.

In spherical polar co-ordinates, the four *eigenfunctions* are

$$\psi_{2,0,0} = \frac{1}{4\sqrt{2\pi}}\left(\frac{z}{a}\right)^{3/2}(2-s)e^{-s/2},$$

$$\psi_{2,1,0} = \frac{1}{4\sqrt{2\pi}}\left(\frac{z}{a}\right)^{3/2}se^{-s/2}\cos\theta,$$

$$\psi_{2,1,1} = \frac{1}{8\sqrt{\pi}}\left(\frac{z}{a}\right)^{3/2}se^{-s/2}\sin\theta e^{i\phi},$$

$$\psi_{2,1,-1} = \frac{1}{8\sqrt{\pi}}\left(\frac{z}{a}\right)^{3/2}se^{-s/2}\sin\theta e^{-i\phi}.$$

We have used

$$s = zr/a,$$

where a is the radius of the smallest Bohr orbit in the hydrogen atom,

$$a = h^2/4\pi^2\mu e^2.$$

The appropriate integrals $I_{n,l,m}$, $J_{n,l,m}$, $S_{n,l,m}$ can be evaluated without great difficulty by a transformation to elliptic co-ordinates. Thus, in terms of ρ and μ, we have

$$r_1r_2 = R^2(\rho^2-\mu^2)/4, \quad d\tau = R^3(\rho^2-\mu^2)d\rho d\mu d\phi/8,$$
$$r_1\cos\theta_1 = R(1+\rho\mu)/2, \quad r_2\cos\theta_2 = R(1-\rho\mu)/2,$$
$$r_1\sin\theta_1 = r_2\sin\theta_2 = R(\rho^2-1)^{\frac{1}{2}}(1-\mu^2)^{\frac{1}{2}}/2.$$

On putting $t = zR/2a$ we have

$$S_{0,0} = e^{-t}(1+t+t^2/3+t^4/15),$$
$$S_{1,0} = e^{-t}(1+t+t^2/5-2t^3/15-t^4/15),$$
$$S_{1,+1} = S_{1,-1} = e^{-t}(1+t+2t^2/5+t^3/15),$$
$$I_{0,0} = (z/2a)\{(1/t) - e^{-2t}(1/t+3/2+t+t^2)\},$$
$$I_{1,0} = (z/2a)\{1/t+3/t^3 - e^{-2t}(t^2+3t+11/2+7/t+6/t^2+3/t^3),$$
$$I_{1,1} = I_{1,-1} = (z/2a)\{1/t-3/2t^3+e^{-2t}(1/2+2/t+3/t^2+3/2t^3),$$
$$J_{0,0} = (z/4a)\,e^{-t}(1+t-2t^2/3+t^3/3),$$
$$J_{1,0} = (z/4a)\,e^{-t}(1+t-t^3/3),$$
$$J_{1,1} = J_{1,-1} = (z/4a)\,e^{-t}(1+t+t^2/3).$$

The suffixes to S, I and J refer to the values of l and m, that of the principal quantum number being omitted as no longer necessary in this paper.

As already pointed out, the expressions for the electronic energies $\epsilon'_{n,l,m}$ and $\epsilon''_{n,l,m}$ are valid only for large values of R. They have actually been calculated for values of $t \geq 3$, that is, for values of R from about 3 Ångströms upwards (when $z = 1$). For small values of R (up to about 0·5 Ångströms), the method of Morse and Stueckelberg [14] can be used. In the intermediate region it is not difficult to make an interpolation.

The change in the value of the electronic energy $E_{n,l,m}$, excluding the term $\Omega(R)$, as the nuclei are brought together from infinity and finally made to coincide, is shown in Table I. The Φ' and Φ'' states (defined in equations (2) and (3)), while degenerate for $R = \infty$, split up as the nuclei approach each other and in all cases the members of the Φ'' set have less energy than the corresponding members of the Φ' set.

This can be seen more clearly from Fig. 1, where the variation of electronic energy (excluding the repulsive part $\Omega(R)$ which is the same for all the levels) is plotted as a function of $R/2a$, assuming the nuclear charge to be unity.[15]

In order to have a notation which relates the electrons in molecules to the levels which they would have on dissociation, we propose to call the lower energy level due to the resonance between the two atomic 1*s* states, a 1*sσ* *molecular* level. The σ has the same meaning as in the Hund-Mulliken notation. The other higher level related to it is denoted by 1*sσ'*. Similarly, the lower levels which would lead on separation to 2*s*, $2p_0$, $2p_{\pm 1}$ atomic states are denoted by 2*sσ*, 2*pσ*, and $2p\pi_{\pm 1}$, and the higher related states by 2*sσ'*, 2*pσ'* and 2*pπ'*.* These levels correspond to the Φ' *eigenfunctions*, which are unsymmetrical in the mid-plane. We shall not find it necessary to use these levels for molecules in their ground states, though they must certainly be used for excited molecules and for an explanation of continuous spectra. The new notation is given in Table I., together with that of Hund and Mulliken for purposes of comparison. The notation has the advantage that it groups together a number of molecular states with the same total quantum number, and with the same symmetry, as, for example, 2*sσ*, 2*pσ*, $2p\pi_+$ and $2p\pi_-$, and these are the only possible members of the group. The next group would consist of 3*sσ*, 3*pσ*, $3p\pi_\pm$, 3*dσ*, $3d\pi_\pm$ and $3d\delta_\pm$, and similarly for groups of higher quantum numbers. The states denoted by the same letters, but with + or − subscripts, are degenerate; the subscript gives the direction of the angular momentum vector.

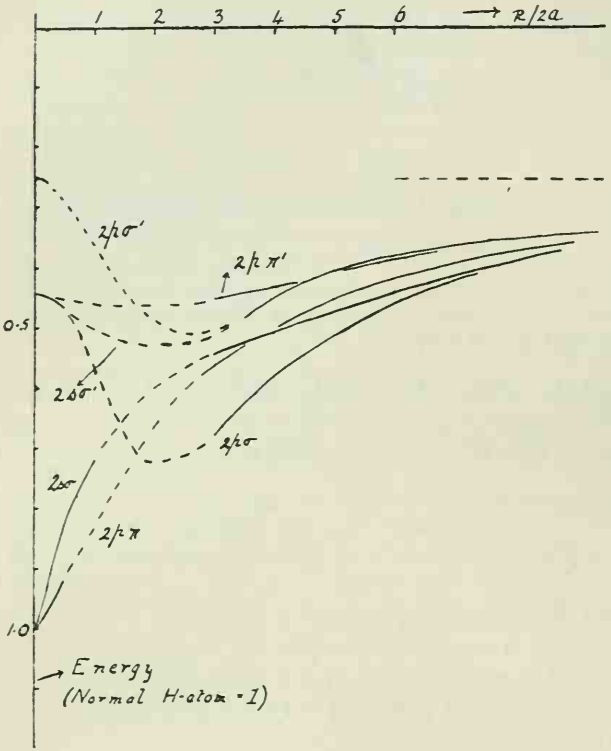


FIG. 1.—The Electronic Energies of some Molecular Levels ($z = 1$).

[15] For the curves for levels of principal quantum number 1, reference should be made to the paper by Morse and Stueckelberg, *loc. cit.* These are not unaffected by the mistake referred to.

* A fuller notation capable of easy generalisation is $\{2p, 2p\}\sigma$, $\{2p, 2p\}\pi'$, etc.

TABLE I.

(Energies of Molecular Levels in Terms of Normal H-atom, E_0.)

Eigenfunction.	R = ∞.		R = 0.		Notation.		
	State in Separated Atoms.	Energy in Separated Atoms.	State in Combined Atoms.	Energy in Combined Atoms.	This Paper.	Hund-Mulliken.	Morse-Stueckelberg.
$\Phi''_{1,0,0}$	$1s$	E_0	$1s$	$4E_0$	$1s\sigma$	$1s\sigma$	$1s\sigma$
$\Phi''_{2,0,0}$	$2s$	$E_0/4$	$2s$	E_0	$2s\sigma$	$2s\sigma$	$2s\sigma$
$\Phi''_{2,1,0}$	$2p_0$	$E_0/4$	$3d$	$4E_0/9$	$2p\sigma$	$3s\sigma$	$3d\sigma$
$\Phi''_{2,1,1}$	$2p_1$	$E_0/4$	$2p_1$	E_0	$2p\pi_+$	$2p\pi_+$	$2p\pi_+$
$\Phi''_{2,1,-1}$	$2p_{-1}$	$E_0/4$	$2p_{-1}$	E_0	$2p\pi_-$	$2p\pi_-$	$2p\pi_-$
$\Phi'_{1,0,0}$	$1s$	E_0	$2p_0$	E_0	$1s\sigma'$	$2p\sigma$	$2p\sigma$
$\Phi'_{2,0,0}$	$2s$	$E_0/4$	$3p_0$	$4E_0/9$	$2s\sigma'$	$3p\sigma$	$3p\sigma$
$\Phi'_{2,1,0}$	$2p_0$	$E_0/4$	$4f$	$E_0/4$	$2p\sigma'$	$4p\sigma$	$4f\sigma$
$\Phi'_{2,1,1}$	$2p_1$	$E_0/4$	$3d_1$	$4E_0/9$	$2p\pi'_+$	$3d\pi_+$	$3d\pi_+$
$\Phi'_{2,1,-1}$	$2p_{-1}$	$E_0/4$	$3d_{-1}$	$4E_0/9$	$2p\pi'_-$	$3d\pi_-$	$3d\pi_-$

The symmetry properties of the *eigenfunctions* of these states in the Wigner-Witmer[16] sense is as follows: The σ, δ, . . . unaccented states are *positive* and the π states negative; the converse is true of the accented states. In general, the unaccented states are positive or negative according as the quantum number of the angular momentum round the nuclear axis is even or odd; the accented states are positive or negative according as it is odd or even.

It is to be observed that the electronic energy ϵ is in every case of the form

$$-(e^2z^2/2a)f(zR/2a),$$

so that $E_n + \epsilon$ is proportional to z^2.

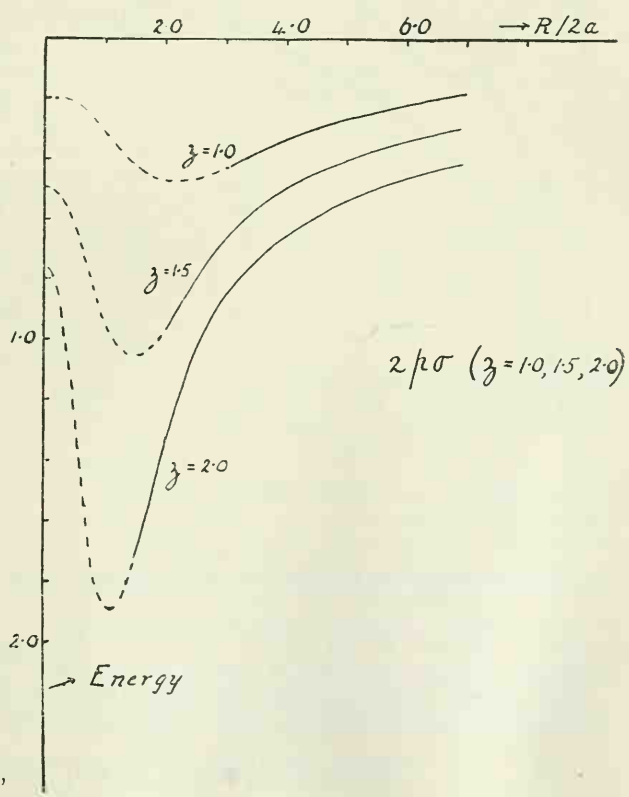


Fig. 2.—The Effect of Nuclear Charge on Molecular Electronic Energies.

[16] Wigner and Witmer, *Z. Physik*, **51**, 859 (1928).

To obtain the electronic energies for different values of z, all that is necessary is to increase the ordinates of Fig. 1 by a factor z^2 and to divide the abscissæ by z. Three typical curves of $2p\sigma$ are given in Fig. 2 for $z = 1{\cdot}0$, $z = 1{\cdot}5$, and $z = 2{\cdot}0$. When only one electron is present, $\Omega(R)$ is merely the electrostatic potential between the nuclei, and the equilibrium distance is given by the minimum of $E + \epsilon + \Omega(R)$. It is not likely that equilibrium is possible for nuclear charges greater than unity. This case (H_2^+) has already been considered by Pauling.[13]

When several electrons are present, progressive changes in z must be made as the states of higher quantum number are considered owing to the screening of the nuclei. To a first approximation, the electronic energies may be regarded as additive, and the total electronic energy considered in relation to $\Omega(R)$ to find the equilibrium internuclear distance. For higher approximations, the interaction of the electrons must be taken into account.

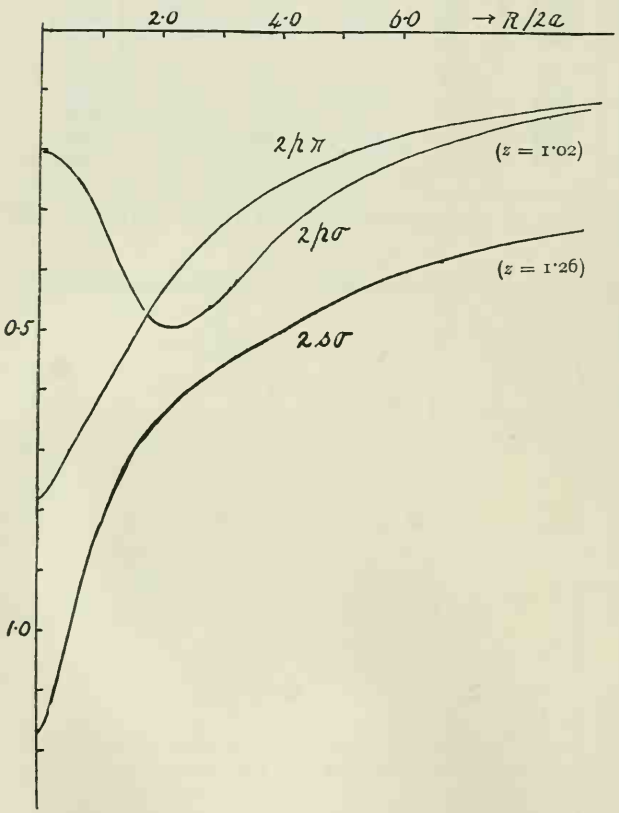


FIG. 3.—The Molecular Levels for the Lithium Molecular Ion.

When only one electron is present, all the molecular states with the same principal quantum number tend to the same value for large internuclear distances, but in more complicated cases this will no longer be the case. If, for instance, we consider an electron in the presence of two Li^+ ions, the $2s\sigma$ tends to the atomic $2s$ state, and this is known to be lower than the $2p$ atomic state, to which the $2p\sigma$ and $2p\pi$ molecular states approximate. The Schrödinger equation for the valency electron of Li may be written

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{r} + V(r)\right) = 0,$$

where $V(r)$ represents the effect of the core, assumed to be spherically symmetrical. The corresponding equation for an electron in the presence of two Li cores is then

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{r_1} + V(r_1) + \frac{Ze^2}{r_2} + V(r_2) + \Omega(R)\right) = 0.$$

The simplest, though roughest, method of taking $V(r_1)$ and $V(r_2)$ into account is to assume that the core electrons have the effect only of providing an imperfect screening of the nucleus, though the amount of screening naturally depends on the state of the outer electron. (In the language of the older quantum theory, the effective nuclear change is greatest for the "*Tauchbahn*" orbits.) We, therefore, combine the terms $Ze^2/r + V(r)$ into a single term and adjust z so that it gives the observed energy level for the atomic states. It is greatest for the s states, and approximates progressively to unity for the p, d, f . . . states.

Fig. 3 shows the effect of such an adjustment for the Li_2^+ case, $z = 1{\cdot}258$ for the $2s\sigma$ state and $1{\cdot}02$ for the $2p\sigma$ and $2p\pi$ states (Li). The $2s\sigma$ molecular state has now less energy than either of the other states for all values of R, and the $2p\sigma$ level is lower than the $2p\pi$ levels for all values of R greater than $4a$, that is, greater than about 2Å. It is unlikely that the equilibrium value of Li_2^+ is less than this, so that we may regard $2p\sigma$ as lower than $2p\pi$. The possible molecular states are shown diagrammatically in Fig. 4, each being represented by a cell which can contain two electrons of opposite spins. In this diagram, we have neglected the unsymmetrical states,[17] $1s\sigma'$, etc., for the following reason. In assigning electrons to the available cells, the first two would obviously be placed in the $1s\sigma$ cell. When three electrons are to be allotted to the levels of principal quantum 1, we prefer not to put two in the $1s\sigma$ level and one in the $1s\sigma'$ level as Hund and Mulliken do ($1s\sigma$ and $2p\sigma$ in their notation), for that distribution appears to give an attraction which does not, in reality, exist. The work of Heitler and London shows that the interaction between three such electrons must be one of repulsion. We therefore assign three electrons to the *atomic* levels ($1s$), and similarly, when there are four electrons. It is to be understood that *the interaction between electrons allotted to atomic levels is always one of repulsion.*

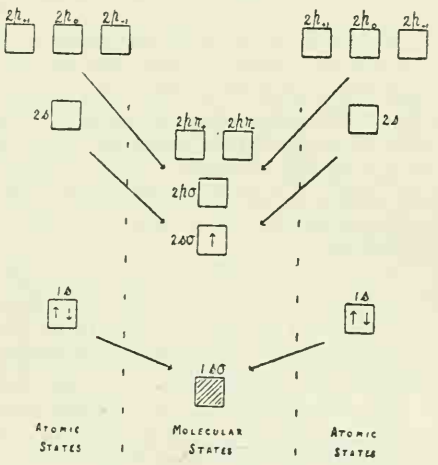


FIG. 4. — Diagrammatic Representation of "Atomic" and "Molecular" Levels. (The electronic configuration of Li_2^+ is shown as an illustration.)

In passing, we note that the *eigenfunction* of three such electrons, taken together, may have positive or negative symmetry in the Wigner-Witmer[16] sense, while the *eigenfunction* of four such electrons can only have positive symmetry. These symmetry properties are important when possible electron transitions are considered, as in N_2^+, dealt with below.

[17] *Cf.* Ludloff, *Z. Physik*, **55**, 304 (1929), who found it unnecessary to consider the unsymmetrical levels in his treatment of the excited states of the H_2 molecule.

We are thus led to the following rules for the assigning of electrons to cells :—

I. Whenever two electrons are placed in a *molecular* cell, the corresponding cell of *each* atom must be left open.

II. Whenever two electrons are allotted to the same atomic cell, the corresponding molecular cell must be excluded.

By a further application of the principles of Heitler and London, we infer a third rule.[18]

III. Whenever two electrons are in a molecular state, they must separate on dissociation so that one goes over to one atom and one to the other, the electron spins being opposite ; and when several pairs of electrons are in molecular states, they must separate so that one electron from each cell goes over to each atom, and the spins of those electrons which go over to the same atom must all point in the same direction.

IV.

In this paper we shall be concerned principally with the ground states of molecules, though some excited states of special interest will also be considered, especially when they illustrate the application of the above rules. We adopt the principle that the normal state of a molecule is that which would be attained by a step-by-step process, in which the charges on the nucleus are increased simultaneously by one unit and then two electrons added consecutively. Each electron is placed in the cell of lowest energy in the diagram of Fig. 4 subject to the rules already formulated.

According to this process, we allot the one electron of H_2^+ to the $1s\sigma$ state, and similarly the two electrons of H_2. As these two electrons form a closed group $1s\sigma^2$, the third electron of He_2^+ must be placed in one of the states of principal quantum 2. The nuclear charges will be partially screened by the inner electrons, and we expect that as in case of Li_2^+ already discussed, the effective nuclear change will be greater for the $2s$ state than for the others. We therefore expect curves of the type shown in Fig. 3, and it seems likely that the third electron must be ascribed to a $2s\sigma$ state, though this cannot be certain without further investigation. In any case, it seems wrong to allot it to the $1s\sigma'$ state, as Weizel[19] has done recently. The fourth electron of He_2, we also allot provisionally to the $2s\sigma$ state. We note, however, that the electronic arrangement $1s\sigma^2$, $2s\sigma^2$ has much greater energy than another arrangement which is possible, *viz.* $1s^2$ (atom A_1) and $1s^2$ (atom A_2). The former has 30 to 40 volts more energy than the latter. This corresponds to the fact that 2 helium atoms normally exist as separate entities, and this condition may be regarded as the normal state. The molecule $1s\sigma^2$, $2s\sigma^2$ dissociates into $\overline{1s}$, $\overline{2s}$ in atom A_1, and $\underline{1s}$, $\underline{2s}$ in atom A_2, the upper and lower lines indicating the electron spin. The atoms are thus in ^3S states.

A similar electronic configuration is possible for Li_2^{++}, though the energy is so high above the alternative configuration $1s^2(A_1)$, $1s^2(A_2)$, that it is not likely to be observed. We therefore regard the latter as the normal configuration, and then place the fifth and sixth electrons in $2s\sigma^2$ states. The seventh and eighth electrons of Be_2 are placed in $2p\sigma^2$

[18] London, *Z. Physik*, **46**, 455 (1928).
[19] Weizel, *Z. Physik*, **54**, 321 (1929) ; **56**, 727 (1929).

states. Both Li_2 and Be_2 should normally be in $^1\Sigma$ states, the molecular ions being of the doublet type $^2\Sigma$.

The ninth electron of Bo_2^+ may be placed in either the state $2p\pi_+$ or $2p\pi_-$, as they are of the same energy. In any case, the spectral term is of the $^2\Pi$ type. The tenth electron of Bo_2 could also be allotted to the same cell giving a $^1\Delta$ term, but here we meet with a new possibility. If one electron is allotted to cell $2p\pi_+$ and one to cell $2p\pi_-$, a resonance is possible between the two states, resulting in a $^3\Sigma$ state and a $^1\Sigma$ state. Of these, the one of highest multiplicity will be lowest as in atoms. It appears, therefore, that Bo_2 should be paramagnetic.

We therefore supplement the three rules already given by a fourth, *viz.* :—

IV. Whenever one electron appears in one molecular cell and one in another, a resonance between molecular states must be considered, and that state will have the lowest energy which corresponds to the greatest multiplicity. To indicate this resonance in Bo_2, we write for the last two electrons $\{2p\pi_+, 2p\pi_-\}$.

Similarly, we expect normal C_2^{++}, if it exists, to be in a $^3\Sigma$ state. When another electron is added to the system, say in $2p\pi_+$, further resonance is prevented, and a $^2\Pi$ term results for C_2^+. When the last electron is added to fill the $2p\pi_-$ cell, all the molecular groups are complete and we have in C_2 a $^1\Sigma$ term. The configuration is then:

$$C_2 : 1s^2(A_1),\ 1s^2(A_2),\ 2s\sigma^2,\ 2p\sigma^2,\ 2p\pi_+{}^2,\ 2p\pi_-{}^2.$$

The products of separation of C_2 from the ground level are then

$$C^* : 1s^2,\ \overline{2s},\ \overline{2p_0},\ \overline{2p_+},\ \overline{2p_-}.$$
$$C^* : 1s^2,\ \underline{2s},\ \underline{2p_0},\ \underline{2p_+},\ \underline{2p_-},$$

which correspond to two excited carbon atoms in the ^5S state, and both tetravalent.

An alternative electron configuration for C_2 is

$$C_2 \text{ (divalent)} : 1s^2(A_1),\ 1s^2(A_2),\ 2s^2(A_1),\ 2s^2(A_2),\ 2p\sigma^2,\ \{2p\pi_+, 2p\pi_-\},$$

which has a valency of two, and the resonance between the two last electrons leads to a $^3\Sigma$ and a $^1\Sigma$ term, the former being the lower. The products of dissociation are

$$C : 1s^2,\ 2s^2,\ \overline{2p_0},\ \overline{2p_+},$$
$$C : 1s^2,\ 2s^2,\ \underline{2p_0},\ \underline{2p_-},$$

both of which are triplet states and must, therefore, be normal C atoms (^3P).

An excited state of C_2, which has approximately the same energy as C_2 (divalent) may be noticed here. If one of the electrons in the $2s$ atomic level be changed to the molecular state $2p\pi_+$ or $2p\pi_-$, the resulting spectral term is a Π term (and may be a singlet or a triplet) as three electrons are distributed between the $2p\pi_+$ and $2p\pi_-$ levels; moreover, the term is *inverted*. The products of dissociation of the configuration, *viz.*, C_2 (excited) : $1s^2,\ 1s^2,\ 2s^2,\ 2s,\ 2p\sigma^2,\ 2p\pi_+{}^2,\ 2p\pi_-$, are

$$C : 1s^2,\ 2s^2,\ \overline{2p_0},\ \overline{2p_+},$$
$$C : 1s^2,\ 2s,\ \underline{2p_0},\ \underline{2p_+},\ \underline{2p_-}.$$

The former of these is a normal C atom, the latter an excited ^5S atom.

As a further example of resonance between molecular states, we note further the excited state of C_2,

$$C_2 \text{ (excited)} : 1s^2,\ 1s^2,\ 2s^2,\ 2s^2,\ \{2p\sigma,\ 2p\pi_+\},\ 2p\pi_-^2,$$

which has an energy rather higher than the divalent C_2 molecule. The resonance between the σ-electron and the π-electron produces a $^3\Pi$ term and a $^1\Pi$ term.

Similarly, the configuration

$$C_2 \text{ (excited)} : 1s^2,\ 1s^2,\ 2p^2_+,\ 2p^2_+,\ 2s\sigma^2,\ \{2p\sigma,\ 2p\pi_-\}$$

gives a $^3\Pi$ term.

In N_2^{++}, as in C_2, we expect to find that the maximum binding arises from two excited N^+ ions, and that the electronic configuration is the same as that given for tetravalent C_2 above. When an electron is added to N_2^{++}, we have the following possibilities,

$$\begin{aligned} N_2^+ \text{ alternative (i)} &: 1s^2,\ 1s^2,\ 2s\sigma^2,\ 2p\sigma^2,\ 2p\pi_+^2,\ 2p\pi_-^2,\ 3s\sigma\ ; \\ \text{(ii)} &: 1s^2,\ 1s^2,\ 2s^2,\ 2s,\ 2p\sigma^2,\ 2p\pi_+^2,\ 2p\pi^2\ ; \\ \text{(iii)} &: 1s^2,\ 1s^2,\ 2s^2,\ 2s^2,\ 2p\sigma^2,\ 2p\pi_+^2,\ 2p\pi_-. \end{aligned}$$

Of these, the first will clearly have the highest energy, owing to the promotion of the last electron into a level of principal quantum number 3. Of the other possibilities, we note that one has a binding due to an *austausch* between six electrons, the other a binding due to only five. It seems likely, therefore, that alternative (ii) is the normal state of N_2. Dissociation from this state leads to :

$$\begin{aligned} N &: 1s^2,\ 2s^2,\ \overline{2p_0},\ \overline{2p_1},\ \overline{2p_{-1}}\ ;\ (^4S, \text{ normal N})\ ; \\ N^+ &: 1s^2,\ 1s,\ \underline{2p_0},\ \underline{2p_1},\ \underline{2p_{-1}}\ ;\ (^5S, \text{ excited } N^+)\ ; \end{aligned}$$

which are the products, deduced by Heitler and Herzberg[11] from the observations of Herzberg.[2] We, therefore, assign the following configuration to N_2,

$$N_2^+ \text{ (normal)} : 1s^2,\ 1s^2,\ 2s^2,\ 2s,\ 2p\sigma^2,\ 2p\pi_+^2,\ 2p\pi_-^2.$$

As the π-group is full, the spectral term must be $^2\Sigma$.

The alternative (iii) given above for N_2^+ is a $^2\Pi$ state, and dissociates into a normal N atom (^4S) and a normal N^+ ion (^3P).

By similar considerations, we are led to consider the ground state for N_2 to be,

$$N_2 \text{ (normal)} : 1s^2,\ 1s^2,\ 2s^2,\ 2s^2,\ 2p\sigma^2,\ 2p\pi_+^2,\ 2p\pi_-^2,$$

which is trivalent, has a closed π group, gives a $^1\Sigma$ state, and separates into two normal N atoms.

V.

At this point, it seems simpler to adopt a different procedure. We begin with the known fact that neon contains a closed group of electrons of total quantum number 2. All the electrons occur in pairs and, as London [20] has shown, no *austausch* is possible if the Pauli Principle is to be preserved. Apart from a weak Van der Waals attractive field due to polarisation, the field is entirely one of repulsion.

The fluorine atom differs from neon in that its nuclear charge is one less and it has one less electron. The electron, which is missing, may be

[20] London, *Z. Physik*, **46**, 455 (1928).

one of six, all of which have the same n and l and the same energy (if the effect of electron spin on the energy is neglected and this is legitimate in F). Instead of considering the five electrons of this type which are present in F, we concentrate on the one which is missing.

To fix ideas, we may picture a fluorine atom in the following way. We add one unit to its nuclear charge and one electron to complete the L group. We then neutralise the additions which have been made by adding a negative charge to the nucleus and a positive mobile particle (with the same mass as the electron) to the electron group. We thus have

$$\text{F} \equiv (\text{Neon-like structure}) + (\text{“ Inverted-hydrogen-system ”}).$$

The latter consists of a *fixed* negative charge and a positive particle in an excited state ($n = 2$, $l = 1$, $m = 1$, 0, or -1). The interaction of two fluorine atoms may thus be represented by the following scheme :—

$$\begin{aligned}\text{F} \rightleftharpoons \text{F} \equiv\ & [\text{Neon} \rightleftharpoons \text{Neon}] \\ & + [\text{“ Inverted-hydrogen ”} \rightleftharpoons \text{“ Inverted-hydrogen ”}] \\ & + 2[\text{Neon} \rightleftharpoons \text{“ Inverted-hydrogen ”}].\end{aligned}$$

The first of these gives repulsion only (neglecting polarisation), the second leads to an *austausch*-resonance attraction, and the third a small attraction owing to the small difference in the polarisation of the neon-like structure by the positive and negative members of the ” inverted hydrogen.” To a close approximation, the latter may clearly be neglected, though we expect a certain perturbation of the molecular levels.[21]

The differential equation for one positive particle alone added to the $F^- + F^-$ system may be written

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}\{E + e^2/r_1 + V(r_1) + e^2/r_2 + V(r_2) + \Omega(R)\}\psi = 0,$$

which is of the same form as that considered for Li_2^+. The $\Omega(R)$ here includes the repulsion of the neon structures.[22] If we make the same crude assumption that $V(r)$ can be represented by a change in the effective charge, then as before we find three possible molecular levels : $2p\sigma$, $2p\pi_+$, and $2p\pi_-$, the last two being degenerate and of higher energy than $2p\sigma$. The first positive particle must therefore be placed in the $2p\sigma$ molecular state, and similarly for the second, though in a quantitative treatment their interaction would have to be considered. This implies that the gaps in the two F atoms, which produce the greatest binding correspond to $n = 2$, $l = 1$, $m = 0$. As the “ gaps ” must have opposite spins, the electrons which are present in those levels must have opposite spins. We can, therefore, write F_2 symbolically in the form

$$F_2 \equiv 1s^2,\ 1s^2,\ 2s^2,\ 2s^2,\ 2p_+^2,\ 2p_+^2,\ 2p^2_{-1},\ 2p^2_{-1},\ 2p_0^4\ [2p\sigma^2],$$

the bracket being used to indicate that it is the absence rather than the presence of electrons, which is regarded as producing the binding ; or, alternatively, we can write

$$F_2 : 1s^4,\ 2s^4,\ 2p_+^2,\ 2p_+^2,\ 2p_-^2,\ 2p_-^2,\ 2p\sigma^2.$$

This gives a $^1\Sigma$ state, and leads to two ^{2}P atoms on separation.

[21] Gale and Monk (*Astroph. J.*, **69**, 77, 1929) find such a perturbation of the F_2 levels, which makes analysis difficult.

[22] Since the forces between two neon atoms are known from gas theory (Lennard-Jones and Cook, *Proc. Roy. Soc.*, A. **112**, 214 (1926), the method here suggested may form the basis of a quantitative treatment of the F_2 molecule. Similar methods could likewise be applied to Cl_2, Br_2 and I_2.

In a similar way, we may consider the formation of O_2 as due to the interaction of four mobile positive particles of charge $+e$ in the presence of two fixed centres of charge $-2e$, with additional central fields of the type $V(r_1)$ and $V(r_2)$, together with the repulsion of two neon-like structures. The first two (with opposite spins) fall into the $2p\sigma$ level, and the remaining two may be distributed as follows: (i) $2p\pi_+^2$, (ii) $2p\pi_-^2$, (iii) $\{2p\pi_+, 2p\pi_-\}$. The last distribution leads to resonance, as found earlier (in Bo_2) and gives rise to two levels, one a $^3\Sigma$ and the other a $^1\Sigma$. The former is lower than any of the other distributions, and so we conclude that it corresponds to normal O_2. The configuration is then

$$O_2 : 1s^2,\ 1s^2,\ 2s^2,\ 2s^2,\ 2p_+^2,\ 2p_-^2,\ 2p\sigma^2,\ \{2p\pi_+,\ 2p\pi_-\}$$

with the following products of dissociation:

$$O : 1s^2,\ 2s^2,\ 2p_+^2,\ \overline{2p_-},\ \overline{2p_0},\ (^3P_0 \text{ term});$$
$$O : 1s^2,\ 2s^2,\ \overline{2p_+},\ 2p_-^2,\ \underline{2p_0},\ (^3P_1 \text{ term}).$$

Both atoms are in their normal states, the other states being ^1D and ^1S, and of higher energy. At first sight, it might appear as though the second oxygen atom had a singlet term, since the spins occur in opposite directions. Actually, however, it is the second member of the triplet ($^3P_1$).

The configuration for O_2, which we have reached, is the same as would be obtained by assuming an *austausch* between the two $2p_0$ electrons, and an *austausch* between the $2p_+$ of one atom with the $2p_-$ of the other. The latter is, therefore, an *austausch* between angular momentum spins instead of between electron spins as usual. We are thus led independently to the same idea as that recently suggested by Heitler,[23] *viz.*, that there are two kinds of unsaturated valencies, which can give rise to molecular binding, one due to an incomplete group of electron spins, and one due to an incomplete group of angular momentum spins.

In a similar way, the electronic configuration of the molecular ions F_2^+ and O_2^+ may be found. The results are given in Table II., where

TABLE II.

THE ELECTRONIC STRUCTURE OF SOME DIATOMIC MOLECULES (GROUND STATE).

	Electronic States.										No. of Binding Electrons.	Molecular Term.	Products of Dissociation.
	1s.	2s.	$2p_0$.	$2p_+$.	$2p_-$.	$1s\sigma$.	$2s\sigma$.	$2p\sigma$.	$2p\pi_+$.	$2p\pi_-$.			
H_2^+						1					1	$^2\Sigma$	$^2S(H)+o$
H_2						2					2	$^1\Sigma$	$^2S+^2S$
He_2^+						2	(1)?				3	$^2\Sigma$	$^3S(He)+^2S(He^+)$
He_2						2	(2)?				4	$^1\Sigma$	$^3S+^3S$
He+He	2+2										o	—	$^1S+^1S$
Li_2	2+2						2				2	$^1\Sigma$	$^2S+^2S$
Be_2	2+2						2	2			4	$^1\Sigma$	$^3P+^3P$
Bo_2	2+2						2	2	1	1	6	$^3\Sigma$	$^4P+^4P$
C_2	2+2						2	2	2	2	8	$^1\Sigma$	$^5S+^5S$
N_2^+	2+2	2+1						2	2	2	6	$^2\Sigma$	$^4S+^5S(N^+)$
N_2	2+2	2+2						2	2	2	6	$^1\Sigma$	$^4S+^4S$
O_2^+	2+2	2+2		2	1			2	1	1	4	$^2\Pi$	$^3P+^4S(O^+)$
O_2	2+2	2+2		2	2			2	1	1	4	$^3\Sigma$	$^3P+^3P$
F_2^+	2+2	2+2		2+2	2+1			2			2	$^2\Pi$	$^2P(F)+^3P(F^+)$
F_2	2+2	2+2		2+2	2+2			2			2	$^1\Sigma$	$^2P+^2P$
Ne+Ne	2+2	2+2	2+2	2+2	2+2						o		

[23] Heitler, *Naturwissenschaften*, 5 July, 1929.

all the results are collected together. Nitrogen might be considered by a similar method, but it has no advantages over that already used, and leads to the same result.

To facilitate comparison of the notation used here with that used previously, Table III. is appended. The symbols with an accent in

TABLE III.—Notation for Molecular Electronic Levels.

Hund-Mulliken.	Morse-Stueckelberg.	New Notation Suggested.
$1s\sigma$	$1s\sigma$	$1s\sigma$
$2s\sigma$	$2s\sigma$	$2s\sigma$
$2p\sigma$	$2p\sigma$	$1s\sigma'$
$2p\pi$	$2p\pi$	$2p\pi$
$3s\sigma$	$3d\sigma$	$2p\sigma$
$3p\sigma$	$3p\sigma$	$2s\sigma'$
$3d\pi$	$3d\pi$	$2p\pi'$
$4p\sigma$	$4f\sigma$	$2p\sigma'$

the last column, being unsymmetrical terms, have not been used in this paper for reasons already given.

VI.

It is not the purpose of this paper to consider the excited states of molecules. These must be left for a later communication, but one case of special interest recently discussed by Mulliken [24] may be noticed here. It is known experimentally that ionisation of N_2 begins at 16·9 volts, and that the negative nitrogen bands ($^2\Sigma - {}^2\Sigma$) are excited at 20·0 volts. These bands are also produced as fluorescent emission when nitrogen is under the action ultra-violet light of short-wave length. These results are easily explained on the basis of the electronic configuration proposed here. The normal configuration for N_2 is given in Fig. 5. The most easily removable electrons are those in the $2s$ atomic levels. At 16·9 volts, one of these is removed and the configuration for N_2^+ in its normal state results.

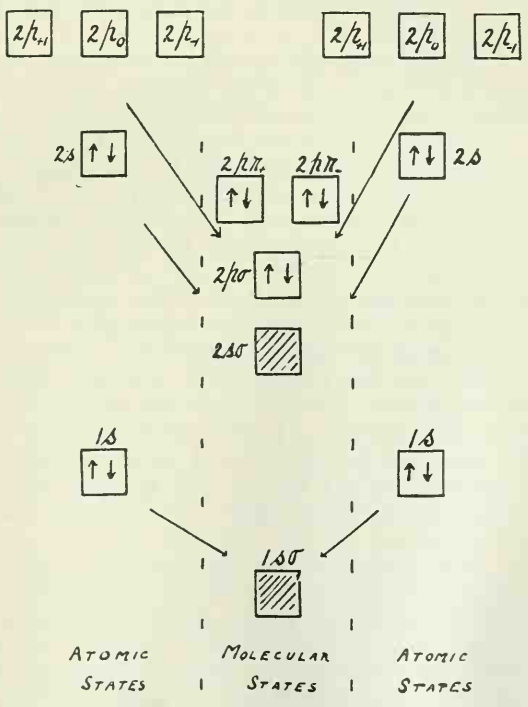


Fig. 5.—The Electronic Configuration of N_2.

[24] Mulliken, *Physical Rev.*, **32**, 206 (1928).

At 20 volts, one of the electrons in the $2p\sigma$ molecular level is removed. This gives a $^2\Sigma$ excited state of N_2^+. Moreover, it is a positive term $^2\Sigma_+$ in the Wigner-Witmer [6] sense, and therefore can only combine with a negative Σ_- term. One of the electrons in the $2s$ atomic level then drops back into the $2p\sigma$ level. This is possible, since the resulting configuration may be negative (see III.). The resultant emission is $^2\Sigma_+ \rightarrow {}^2\Sigma_-$, which are the observed negative nitrogen bands.

Furthermore, as the ground level of N_2^+ is of negative symmetry in the electrons, it follows that the even rotational terms should be strongest, while in the $^2\Sigma_+$ excited state, the odd rotational levels should be strongest.[25] This is in accordance with observation, for it is found that, the transition $1 \rightarrow 0$, $3 \rightarrow 2$, . . . $1 \rightarrow 2$, $3 \rightarrow 4$, . . . are stronger than those between $2 \rightarrow 1$, $4 \rightarrow 3$, . . . and $0 \rightarrow 1$, $2 \rightarrow 3$, . . .

[25] *Cf.* Hund, *Z. Physik*, **51**, 783 (1928).

THE ELECTRONIC LEVELS OF H_2.

By Professor O. W. Richardson, King's College, University of London.

(*Communicated to the Society on 24th September*, 1929.)

Great progress has recently been made in the study of this spectrum, and I propose to give the Conference a brief account of the present state of our knowledge of the electronic levels, which are very interesting.

The bands which rest on the ground state of H_2 do not occur in the visible spectrum but lie in the Lyman region. Some of them were first observed by Lyman and shown later, by Witmer, to consist of a long progression with the same initial states. A large number of other bands were found by Werner. The absorption spectrum of H_2 was discovered by Dieke and Hopfield, who showed that it contained two band systems going from the ground level which they called "A" to a level "B" about 90,000 wave numbers higher and to a level "C" about 99,000 wave numbers higher respectively. The emission bands found by Werner are the transitions $C \rightarrow A$ and those found by Lyman part of the system $B \rightarrow A$. Both systems have been analysed by Hori,[1] who showed that the $C \rightarrow A$ bands consisted of P, R, and Q′ branches. He supposed that the $B \rightarrow A$ bands consisted of an R branch and an identical P and Q′ branch. If, however, this Q′ branch is regarded as a fiction, so that the bands consist of an R and a P branch his analysis is correct.

In its main outlines the spectrum of H_2 undoubtedly possesses a structure very similar to the spectra of atomic He and molecular He_2. We therefore expect the ground state of H_2 to be specified by the notation $(1s)(1s)$ $S^1\Sigma$, and this agrees with the fact that H_2 is diamagnetic. Assuming that only one electron is excited, there are three states of electronic principal quantum number 2 which can go down to $1s^2S^1\Sigma$. These are $(1s)(2p)P^1\Pi_a$, $(1s)(2p)P^1\Pi_b$, and $(1s)(2p)P^1\Sigma$. We therefore identify the two levels in C which give rise to the P and R and the Q′ branches, respectively, as $1s\ 2p\ P^1\Pi_{a,\,b}$ and the single level in B as $(1s)(2p)P^1\Sigma$. All the known facts are in agreement with this classification.

Since there is no evidence from the energy values that in any of the known levels more than one electron is excited, I shall contract this notation in the remainder of this paper, omitting the $1s$ which is common to all states and the letter such as P which describes the L value for the whole molecule. This is uniquely determined by the letter p which described the l value for the excited atom. Thus $(1s)(2p)P^1\Sigma$ becomes simply $2p^1\Sigma$.

Between 1924 and 1927 I found some of the bands which end on the B or $2p^1\Sigma$ level, and in the last year or so Dr. Davidson and I,[2] thanks to the excellent wave-length measurements of Gale, Monk, and Lee, have been able to effect a complete analysis of the bands which end on this level, which, in our papers, is called 2^1S. We find that there are seventeen higher electronic levels giving rise to band systems with transitions to this level. Of these one has an effective principal quantum number close to 2, twelve lie between 2·9 and 3·4 and five between 3·9 and 4·1. These levels we have designated provisionally by the symbols such as 3^1C etc., which are shown, together with the transitions which they undergo, in Fig. 1. Some of these levels have since been confirmed by the independent work of Finkelnburg and Mecke.[3] It is possible that there may be still other levels giving weak transitions to $2p^1\Sigma$, but we believe we have found all those which have any appreciable strength.

These levels differ very greatly in their properties and in the characteristics of the band systems to which the transitions from them to $2p^1\Sigma$ give rise. The band systems going from 3^1A, 3^1B and 3^1C to $2p^1\Sigma$ are the most extensive, each having four initial and eight or nine final vibrational states. These systems include the strongest lines in the secondary spectrum of hydrogen in the visible. The bands of maximum intensity on the usual $n'n''$ plot lie on a broad parabola with a very weak minimum along the axis. In the case of one of them, $3^1B \rightarrow 2p^1\Sigma$, the potential energy for both states as a function of the distance between the nuclei has been calculated and the intensity distribution can be deduced [4] from this by Condon's method. The result shows a good agreement between theory and observation. These bands all show well marked uncoupling effects of the type noted by Curtis, Dieke, and Weizel in the He_2 spectrum.[11] The system $3^1C \rightarrow 2p^1\Sigma$ is distinguished from the others by the fact that its lines respond to the Zeeman effect. The initial state has no missing rotational levels so that it is a Σ state and it shows very pronounced uncoupling effects. In fact all its properties are in harmony with the view that this upper state is $3d^1\Sigma$ which is one of the p.q.n.* = 3 states which should give strong transitions to $2p^1\Sigma$. The system $3^1A \rightarrow 2p^1\Sigma$ has only P and R branches whilst $3^1B \rightarrow 2p^1\Sigma$ has only Q. Both initial levels have the lowest rotational level absent so that they are evidently Π levels. Each shows some uncoupling and they are very close together so that there is very little doubt that 3^1A is $3d^1\Pi_a$ and 3^1B is $3d^1\Pi_b$. This pair of levels should also give strong transitions to $2p^1\Sigma$. There should be two other $3d$ levels which combine with $2p^1\Sigma$. The bands should be weak and I think they are represented by the two progressions which start at λ4097Å and 4143Å. These are the only progressions which have enough missing rotational levels for Δ levels, so I think that they together constitute $3d^1\Delta a \rightarrow 2p^1\Sigma$ and $3d^1\Delta b \rightarrow 2p^1\Sigma$.

* To save type I write p.q.n. for principal quantum number.

A p.q.n. 3 level which should have strong transitions to $2p^1\Sigma$ is $3s^1\Sigma$. On various grounds either 3^1K, 3^1N or 3^1O might be assigned to this level. 3^1K is more in the position to be expected for it, but the rotational structure is peculiar and if the $2'$ progression is correctly placed in this

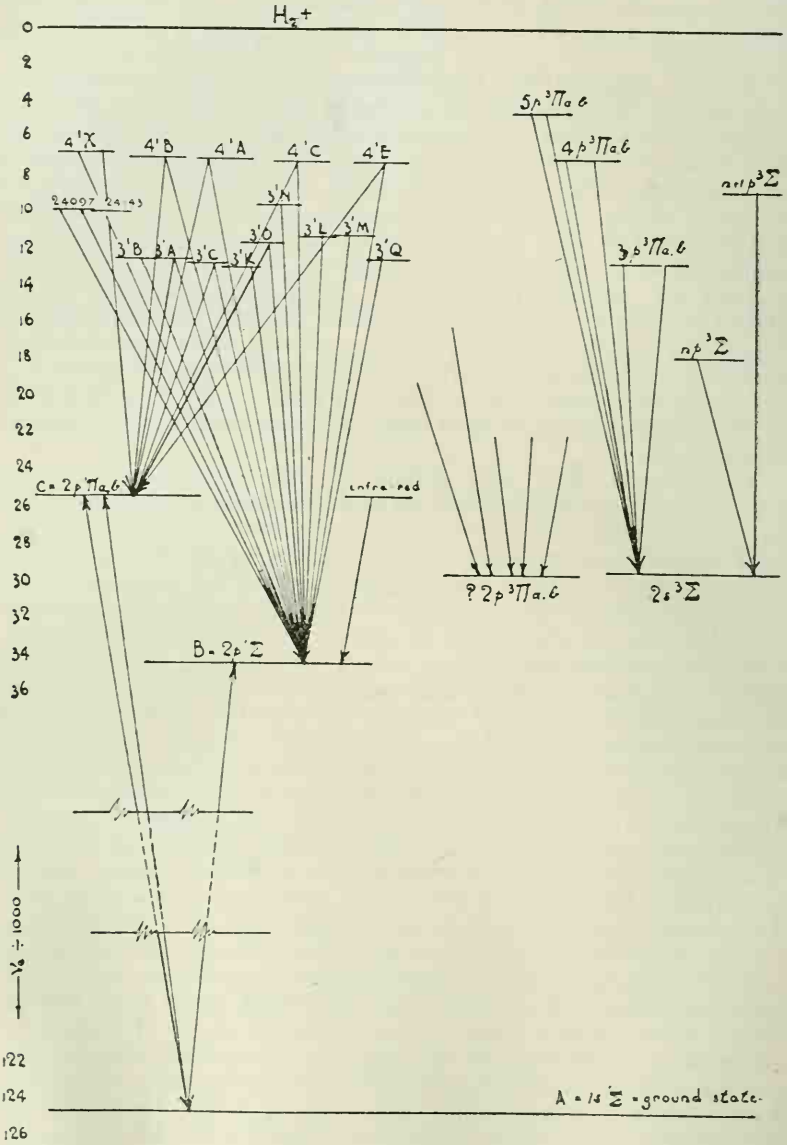


FIG. 1.

system, it shows strong uncoupling which is not to be expected for an $s\Sigma$ level. The rotational structure of 3^1O and the intensity distribution in the system $3^1O \rightarrow 2p^1\Sigma$ look more reasonable for $3s^1\Sigma$, but the band system is rather weak and the position of the level is high.

Before proceeding with the further discussion of the classification of the electronic levels, it will be well to mention some general features of importance which govern the whole structure of the spectrum. The successive lines of every branch of every band have an alternation in intensity. This arises from a similar alternation in a ratio of 3 to 1 in the weights of successive rotational levels. This is an effect of nuclear spin, the weak levels, marked *s*, having antiparallel and the strong levels, marked *a*, having parallel nuclear spins. These spins are space quantised to the rotational axis with the result that the *a* levels have three times the weight of the *s* levels. Considerations of the symmetry properties of the proper functions of the molecule due to Heisenberg [5] and Hund [5] require that *s* levels only combine with *s* levels and *a* with *a*. It is a fact that the spectrum consists of two alternating sets of non-intercombining levels of just this kind and the weight ratio is 3 to 1. The selection rules in fact are $\Delta K = 0$ or ± 1 and $s \rightleftharpoons a$ prohibited.

These selection rules require that a transition between any two single electronic levels should give rise either to Q branches alone or to P and R branches without Q branches. Leaving out of account 4^1A, 4^1B, $4^1\chi$ and the progressions about 4097 and 4143, about which there is an element of uncertainty owing to the meagreness of the data, all the transitions to $2p^1\Sigma$ shown in Fig. 1 give rise to *P* and *R* branches without Q branches except $3^1B \rightarrow 2p^1\Sigma$ which gives rise to Q branches only.

Returning now to the classification of the levels which combine with $2p^1\Sigma$ let us consider first the level at about 25,300 wave numbers, called "infra-red" because the transitions give rise to the strongest lines in the infra-red part of the spectrum. It is unlikely that the whole of this system is known, but enough is known to be certain that the effective p.q.n. of this level is not much more than 2. There should be a level with p.q.n. 2 which combines with $2p^1\Sigma$ namely, $2s^1\Sigma$. The initial level of the infra-red system possesses an abnormal rotational structure resembling that arising from uncoupling, but I am inclined to the view that this is some other kind of abnormality and that this level really is $2s^1\Sigma$, especially as the transitions to $2p^1\Sigma$ from it are very strong.

I shall now consider the five levels whose effective p.q.n. lies between 3·9 and 4·1. The energy of these levels is very high, so that it is not surprising that for four of them only the $0' \rightarrow n''$ progression is known for the systems which go down to $2p^1\Sigma$. One has the $1' \rightarrow n''$ progression in addition. There is little doubt that these initial vibration numbers are correctly assigned, on account of the intensity distribution of the bands. The strongest systems are $4^1B \rightarrow 2p^1\Sigma$, $4^1C \rightarrow 2p^1\Sigma$, and 4^1E to $2p^1\Sigma$, the systems arising from $4^1\chi$ and 4^1A being notably weaker. The detailed elucidation of these systems is very difficult as they are very closely interwoven with each other and many of the bands are mixed up with stronger bands of other systems. In addition faint lines may be lost in the continuous background in which most of them lie. The published account is thought to be wrong in some particulars and the whole question of these five levels requires reconsideration. The decision, if I had to decide, I should make at the moment is 4^1A and $4^1B = 4d^1\Pi$a and $4d^1\Pi$b, $4^1\chi = 4d^1\Delta$a or $4d^1\Delta$b and either 4^1E or 4^1C is to be assigned either to $4d^1\Sigma$ or $4s^1\Sigma$ respectively. The main point I wish to make is that at this stage, *i.e.* at p.q.n. 4, there are no more known levels than the current theories account for. Of course this may only mean that there are others which are weak and have not yet been found.

This is not the case in the neighbourhood of p.q.n. = 3. We have accounted, at any rate provisionally, for 3^1A (effective p.q.n. = 2·957) as $3d^1\Pi_a$, 3^1B (e.p.q.n. = 2·960) as $3d^1\Pi_b$, 3^1C (e.p.q.n. = 2·932) as $3d^1\Sigma$, the progressions at 4097 and 4143 Å. (e.p.q.n. = 3·32) as $3d^1\Delta$ and one of either 3^1K, 3^1O or 3^1N as $3s^1\Sigma$. 3^1Q (e.p.q.n. = 2·958) might possibly be one of the levels of $3p^1\Pi_{a,\,b}$, which should not combine with $2p^1\Sigma$, as it consists of only a single weak progression and has the lowest rotational level missing. We are still left with 3^1L (e.p.q.n. = 3·118), 3^1M (e.p.q.n. = 3·138), and two out of 3^1K (e.p.q.n. = 2·913), 3^1O (e.p.q.n. = 3·07), and 3^1N (e.p.q.n. = 3·403), probably 3^1K and 3^1N, in all, four electronic levels lying outside the scheme of s and d (or S and D) levels which should combine with $2p^1\Sigma$ according to theory. This is undoubtedly a fact of importance. All these four levels are very similar: they are all Σ levels, *i.e.*, they give rise only to P and R branches in the transitions to $2p^1\Sigma$ and they have no missing levels, they all show the same abnormal type of rotational structure which suggests strong uncoupling and they all give rise to band systems in the transitions to $2p^1\Sigma$ which have a more complicated intensity distribution than the others. They are weaker than the $3d \rightarrow 2p^1\Sigma$ complex, but there are some very strong bands among them. It is conceivable that by some rearrangement of the initial vibrational levels the number of these " extra " systems might be reduced, but I do not believe it would be possible to contract it to less than 3 if at all.

It will be asked how we know that the levels have the effective quantum numbers assigned to them. This was ascertained by taking the null frequencies of the band systems $3^1B \rightarrow 2p^1\Sigma$ and $4^1B \rightarrow 2p^1\Sigma$ and assuming they were given by a Rydberg formula $\nu = A - \frac{109678 \cdot 3}{(m-x)^2}$, $m = 3, 4$. This gave $x = 0 \cdot 0395$ and $A = 34{,}365$ as the interval between $2p^1\Sigma$ and H_2^+ (the limit of the series). The interval 90,204 between $2p^1\Sigma$ and $1s^1\Sigma$ is got from Hori's analysis of the ultra-violet bands, as also is the interval 99,205 between $2p^1\Pi$ and $1s^1\Sigma$. By adding 34,365 to 90,204 we get 124,569 as the interval between $1s^1\Sigma$ and the ground level of H_2^+. As all the other levels go down to $2p^1\Sigma$ their intervals from H_2^+ are got by subtracting the null frequencies of the band systems from 34,365 and the effective quantum numbers by assuming a Rydberg formula to apply to them. These calculations give 15·381 volts for the spectroscopic ionisation potential of H_2. The ionisation potential determined by electrical methods should be higher owing to the vibrational energy given to the molecule and is 15·9 volts. The value 15·381 combined with Burrau's [6] computation of the negative energy of H_2^+ on the wave mechanics gives for the heat of dissociation of H_2 4·465 volts compared with Witmer's extrapolation from the frequency intervals of the $1s^1\Sigma$ level 4·34 volts and Bichowsky and Copeland's [12] direct measurement 4·55 ± 0·16 volts. We also find from the H_2 band spectra data that ω_0 and $x\omega_0$ for H_2^+ are 2280 and 60 wave numbers respectively. These are identical with the values computed by Burrau. There is no other confirmation of the application of the wave-mechanics to a problem involving more than two bodies which approaches this in accuracy.

I have recently [7] found the band systems which go down to the C level of Dieke and Hopfield ($2p^1\Pi$). The upper levels are identical with one or other of the levels which go down to $2p^1\Sigma$. The transitions which have been observed are indicated by the arrows in Fig. 1. All

the five levels with effective p.q.n. = about 4 go down to this level. Most of the bands from these are in the green part of the spectrum. Band systems corresponding to transitions from 3^1A 3^1C and 3^1O to $2p^1\Pi$ also certainly occur. These bands lie in the infra-red. All the bands are weak compared with the corresponding bands ending on $2p^1\Sigma$. It is possible that more of the levels with p.q.n. about 3 go down to $2p^1\Pi$, but that the corresponding infra-red lines are so faint as to have escaped notice. The bands have P, Q′ and R branches corresponding to the double character of the $2p^1\Pi_{a,\,b}$ level. As a rule the Q′ branch is strongest and the P branch weakest. The final term differences, both vibrational and rotational, agree with Hori's values for the $2p^1\Pi$ level to the accuracy of the ultra-violet data. This shows that the upper level of the infra-red band system ending on $2p^1\Sigma$ which I have provisionally allocated to $2s^1\Sigma$ is something different from $2p^1\Pi$ although it lies very near to it.

We come now to a very important series of strong band systems which I first succeeded in arranging in 1926.[8] These systems all have a common final level and their null frequencies follow a Rydberg formula. The e.p.q.n.'s of the initial levels are 2·937, 3·942, 4·95, and 5·95 respectively, that for the final level is 1·933. All bands have PQ′ and R branches with Q′ strongest and P weakest. Analysis shows that this is due to the upper levels being double and that neither initial nor final levels show appreciable uncoupling phenomena. The initial terms are almost identical with the initial terms of the principal series of the orthohelium line spectrum with the same p.q.n. The properties of the initial level show that these are $mp\Pi$ levels, $m = 3, 4, 5$. The final level has the properties of a Σ level and if the initial levels are $mp\Pi$, we expect this to be $2s\Sigma$. It might be either $2s^1\Sigma$ or $2s^3\Sigma$ as it does not combine with the ground level of H_2 and neither of these would. However, we already have another candidate in the field for the $2s^1\Sigma$ level and in view of the fact that the $mp\Pi$ terms lie so very close to the orthohelium line spectrum terms already mentioned, I propose to call these terms $mp^3\Pi$ and $2s^3\Sigma$ terms respectively. This assumed theoretical triplicity has no observational support, all the lines being single so far as is known. However, the corresponding He_2 triplets are very narrow and those of H_2 should be still narrower. The determination of the fine structure of the lines is also made difficult by the lightness of the molecule which gives a large Doppler effect broadening.

The $s\Sigma$ nature of the lower level of the foregoing band systems is confirmed by the existence of two other levels [9] which go down to it. These have e.p.q.n.'s = 2·485 and 3·53 respectively. The transitions to $2s^3\Sigma$ give rise to systems whose bands have P and R but no Q branches; accordingly it is a Σ level and I propose to call it $mp^3\Sigma$. The values of m might be either 2 and 3 or 3 and 4. There is something to be said on both sides of this question, so we have to leave it undetermined for the present.

Within the last few days I have found evidence of the existence of a number of band systems with a common final electronic level in the neighbourhood of 29,500 wave numbers (e.p.q.n. about 1·93). It is not possible as yet to say much about the initial levels except that there seem to be about half a dozen of them. So far as I have got the facts are in harmony with the view that the final level is $2p^3\Pi_{a,\,b}$.

It is sometimes urged against the suggested assignment of these bands to the triplet system that the triplet system should be stronger than the singlet system as in helium, whereas the lines of the α etc.

bands though strong are much weaker than those of the ^1C and $^1B \rightarrow 2p^1\Sigma$ bands. I think there is little force in this objection as there is experimental evidence that the two sets of systems are excited in different ways, the par system (singlet) mainly by direct electron impact excitation of neutral H_2 and the ortho-system (triplet) by recombination of H_2^+ and electrons.[10]

In the following table I have collected together the more important constants and properties of the different levels so far as they have been ascertained or estimated.

TABLE I.

All the data in this table are based on the formulæ of the old quantum mechanics. ν_e is the n, $m = 0$ electronic term in wave numbers measured from the series limit which is the ground state of H_2^+. The values have been actually measured from $2'S = 2p'\Sigma = 34{,}365$ (Richardson and Davidson, *Roy. Soc. Proc.*, **A. 123,** 483, 1929) or $2^3S = 2s^3\Sigma = 29{,}340$ (Richardson, *ibid.*, **113,** 398, 1926).

Level.	ν_e.	den.	E.	D.	ω_0.	$\omega_0 x$.	$2B_0$.	$r_0 \times 10^8$.	ϵ.	σ.
1^1S Dieke and Hopfield's A	124569	0·934	31·54	4·465	4262	113·5	—	0·76	0	0
2^1S ,, ,, B	34365	1·959	20·40	3·47	1337·726	19·54	38·91	1·313	0	0
2^1P ,, ,, C	25475	2·075	19·30	2·37	2380	66·5	59	1·06	—	—
$2^3P = 2p^3$IIa, b	29500_0	1·93	—	—	—	—	—	—	—	1
2^3S	29340	1·933	19·78	2·85	2594	70·5	66·773	0·998	0	0
$np^3\Sigma$ (of Fig 1)	17733	$2·48_5$	18·35	$1·42_5$	2130	67	53·08	1·119	0	0
3^3P (Q)	12719	2·937	17·73	$2·68_5$	2307·5	65·01	59·09	1·061	0	1
3^3P (R')	12719	2·937	17·73	$2·68_5$	2307·5	—	59·65	1·056	0	1
3^1A	12546	2·957	17·70	$2·65_5$	2143·00	40·33	ca.40*	—	$-\frac{1}{2}$	0
3^1B	$12515·_5$	2·960	17·70	$2·65_5$	2175·06	77·84	56·6† ca.50*	—	$+\frac{1}{2}$	1
3^1C	$12758·_5$	2·932	17·73	2·68	2340·60	114·85	56·6† ca.40*	—	$+1\frac{1}{2}$	0
3^1K	$12937·_5$	2·913	17·755	2·71	2239	$6·_4$	21·8*	—	0	0
3^1L	$11305·$	3·118	17·55	2·50	ca. 1830	—	19·4*	—	0	0
3^1M	$11173·$	3·138	17·53	2·48	219_3	1_6.	26 *	—	0 ?	v
3^1N	9469	3·403	17·33	2·28‡	ca. 2000		36 *	—	0	0
3^1O	11614	3·07	17·59	2·54	2414	124	59 *	—	0	0
3^1Q	12525	2·958	17·70	2·65	—	—	75 *	—	0	?
λ4142·801 (upper)	10000	3·31	17·39	2·34‡	—	—	75 * or 52	—	$+1\frac{1}{2}$?	>1
λ4097·433 (upper)	9935	3·328	17·38	2·33‡	—	—	—	—	0 ?	>0
$(n+1)p^3\Sigma$ (of Fig. 1)	8810	3·53	17·25	2·20	2184 ?	—	57·04	1·114	$\frac{1}{2}$	0
4^3P (Q)	7067	3·942	17·03	2·64	2276·5	6_0.	58·80	1·064	0	1
4^3P (R')	7067	3·942	17·03	2·64	—	—	58·575	1·066	0	1
4^1A	7008	3·956	17·02	2·63	—	—	about 60	about 1·05	$-\frac{1}{2}$	0
4^1B	$6991·_5$	3·961	17·02	2·63	ca. 2200	—	about 60	about 1·05	$+\frac{1}{2}$?	0
4^1C	$7152·_5$	3·915	17·04	2·65	—	—	about 60	about 1·05	$+1\frac{1}{2}$	1
4^1K	$6761·_5$	4·03	16·99	2·60	—	—	about 60	about 1·05	$+2\frac{1}{2}$?	2
4^1E	7187	3·91	17·05	2·66	—	—	about 60	about 1·05	2 ?	1
5^3P	4493	4·96	16·71	2·63	2251	5_8	5_7	—	—	—
6^3P	3107	5·95	16·55	2·63	2236	5_7	5_7	—	—	—
Infra-red system (upper state) §	$25300·$	$2·08_4$	19·28	2·35	$2350·$	1_{00}.	ca. 50	ca. 1·2	0	0
Infra-red system (upper state)‖	21009	2·286	$18·7_5$	$3·70_5$	1900	—	40·	$1·_3$	0	0
H_2^+	0	∞	16·16	2·62	2280	60	59	1·06	—	—

* Value for m small.
† Value for m large.
‡ These data assume that the relevant level (3^1N, upper of λ4142·801 or upper of λ4097·433) is a 3-electronic level.
§ These data assume the upper level to be a $n = 2$ electronic level and that 11310 is the $n' = 1$ band.
‖ These data assume the upper level to be a $n = 3$ electronic level and that $13402·1$ is the $n' = 0$ band. It seems pretty certain from these figures that the assumption (electronic $n = 3$) is untenable.

Dieke and Hopfield's A and C involve Hori's measures, the remainder rest on the measures of Gale, Monk, and Lee. " den " is the value of z if $\nu_e =$ Rydberg constant $\div z^2$. E is the negative total energy and D the heat of dissociation of the molecule in the specified state, expressed in equivalent volts. ω_0 is the vibration frequency (wave-numbers) at infinitesimal amplitude. $\omega_0 x$ and $2B_0$ are the usual band system

constants. r_0 is the equilibrium nuclear separation. ϵ is the constant required to express the rotational terms as $B(j-\epsilon)^2$ with j half-integral. σ is the number of missing rotational levels. v means variable. Uncertain figures are depressed. Owing to peculiarities of the electronic levels many of the band constants, especially those of the upper levels of bands ending on $2\,{}^1S$ are estimated subject to particular assumptions. For a complete interpretation of the table reference should be made to 2, 4, 7, 8 and 9.

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THE BAND SPECTRUM OF HELIUM.*

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Introductory.

When a discharge of suitable intensity is passed through pure helium at a pressure of a few cms. of mercury a complex spectrum is excited which must be attributed to the molecule He_2. It has been the subject of extensive investigations in the visible and near ultra-violet regions ($\lambda\lambda 7000 - 3000$), and has now been resolved almost completely into its constituent bands. Since these present some characteristics of great interest, and the details of their analysis are distributed over a number of papers by various workers, it appears desirable to collect and survey the results obtained.

Attention may first be directed to some of the special features which distinguish this from most other band spectra. They are as follows :—

(1) It is closely related to the He atomic spectrum, all the terms of the latter having molecular counterparts, but there are a number of additional terms peculiar to the molecule.

(2) The electronic terms are divisible into two non-combining systems just as in the case of He, and probably also of triplet and singlet character.[38] They may be similarly designated ortho- and par-, or distinguished by the usual triplet and singlet notation, according to convenience. The latter system is an exact replica of the former, differing only in its lower intensity, so that for the most part we need only consider here the ortho-He_2 system, which is much more completely known. A much greater number—some 40—of electronic terms have been identified than in any other band spectrum, except that of hydrogen.

(3) The bands are of unusual appearance in several respects. The spacing is wide, and there are comparatively few lines in each branch, so that heads are the exception rather than the rule. In many cases they are not capable of being represented even approximately by a parabolic formula, and the intensity relationships between the branches are apt to be very peculiar. These circumstances, together with the occurrence of a number of perturbations, are responsible for the difficulty which has been found in analysing the spectrum. There are two compensating features, however. One is the comparative weakness of all bands involving vibration states other than the fundamental, and the other is the absence of alternate rotational levels, whereby half of the lines are suppressed.

(4) The electronic (W_e), vibrational (W_k), and rotational (W_r) energies of the molecule do not differ so widely as is commonly the case. Thus W_e may be as low as 1000 cm.$^{-1}$, W_k is about 1700 for the first vibrational level, and W_r may be as much as 3000. The usual condition that $W_e \gg W_k \gg W_r$ is thus not always applicable here, and it is not permissible to regard the total energy as the sum of three separate parts. Interaction between them may, and does at times, become important.

* Communicated to the Faraday Society on 24th September, 1929.

The Electronic Terms.

There is one obvious series of bands in the ${}_0He_2$ system which follows a Rydberg law,[3] and is the analogue of the ortho-He principal series, $n^3P \rightarrow 2^3S$. This has been followed as far as $n = 10$, whilst none of the other series, which are considerably weaker, extend beyond $n = 6$ at present. Nevertheless, it has been possible to evaluate the terms with satisfactory accuracy. They fall into three groups on the basis of their combining properties, and a variety of evidence goes to show that $l = 0$, 1 and 2 for these groups. The first, S, is single; the second comprises two term-types, U and P; the third three, Z, XY and D.* The subdivision is explicable on Hund's theory as arising from the different possible values of σ_l, the component of l along the nuclear axis. It is clear from considerations of missing lines and from the general properties of the terms that for S, $\sigma_l = 0$; for U and P, $\sigma_l = 0$ and 1 respectively; and for Z, XY and D, $\sigma_l = 0$, 1 and 2 respectively. We may therefore substitute for the empirical scheme of notation one based on theory, using the letters σ, π, δ to denote $l = 0$, 1, 2 and Σ, Π, Δ to denote $\sigma_l = 0$, 1, 2. A detailed comparison of the two schemes will be found in Fig. 5.

Only combinations for which $\Delta l = \pm 1$ have been observed, and in the region studied we have only to do with transitions to the levels $2\sigma\Sigma$, $2\pi\Sigma$, and $2\pi\Pi$. It should be remarked that whereas the l classification is quite general, the σ_l classification strictly applies only in the case of low n values; the question of its breakdown will be discussed later.

The term values and effective quantum numbers for ${}_0He_2$ are collected in Table I. The latter are to be found by adding the lower number in

TABLE I.—Electronic Terms and Effective Quantum Numbers in ${}_0He_2$.

n.	2.	3.	4.	5.	6.
$\sigma\Sigma$	34,302 − 0·212	13,893 − 0·190	7,524 − 0·182	4,708 − 0·173	3,223 − 0·166
$\pi\Sigma$	23,394 + 0·163	— —	— —	— —	— —
$\pi\Pi$	29,517 − 0·072	12,795 − 0·072	7,109 − 0·072	4,516 − 0·072	3,122 − 0·073
$\delta\Sigma$	— —	12,734 − 0·065	7,080 − 0·064	4,488 − 0·057	3,103 − 0·055
$\delta\Pi_b$	— —	12,533 − 0·042	6,992 − 0·039	4,431 − 0·025	3,053 − 0·006
$\delta\Pi_a$	— —	12,531 − 0·042	7,009 − 0·044	4,417 − 0·017	— —
$\delta\Delta_b$	— —	12,081 + 0·013	6,818 + 0·011	4,389 − 0·001	3,057 − 0·010
$\delta\Delta_a$	— —	12,081 + 0·013	6,818 + 0·011	4,437 − 0·028	— —

* This notation is the empirical one developed during the analysis. It was not at first recognised that the X and Y levels are really one, being related to one another in the same way as the two components of the D level.

each space to the integer at the head of the column, that is to say, it is the quantum defect which is tabulated. The corresponding data for ${}_p\mathrm{He}_2$ are much less complete; they have been given in Table II. of reference 20, and are not repeated here, since comparatively few additions would be necessary.

The $\pi\Pi$ term is double, but the separation of the electron terms is hardly appreciable. The behaviour of the $\delta\Pi_a$ and $\delta\Pi_b$ levels is peculiar in that for $n = 3$ they are practically coincident, for $n = 4$ they are well separated, but for $n = 5$ they have crossed over. The only term sequence of which no members have as yet been found is $\pi\Sigma$ of ${}_p\mathrm{He}_2$, but there is no reason to suspect that this does not occur.

If the analogy with the atomic case were complete, we should expect to find series in the Lyman region associated with the limit 1^1S, but in this case two series instead of one, namely $n\pi^1\Pi \rightarrow 1\sigma^1\Sigma$ and $n\pi^1\Sigma \rightarrow 1\sigma^1\Sigma$. Some radiations probably of a band nature have been observed in this region, and Sommer [17] has suggested that the strongest of these, near λ600 Å., may be $2\sigma^3\Sigma \rightarrow 1\sigma^1\Sigma$. One would have expected $2\pi^1\Pi \rightarrow 1\sigma^1\Sigma$ to be the strongest band in this region, and so far as position is concerned the band in question might equally well be interpreted in this way. The difficulty with either interpretation is the absence of the next series member, $3\sigma^3\Sigma \rightarrow 1\sigma^1\Sigma$ or $3\pi^1\Pi \rightarrow 1\sigma^1\Sigma$, either of which would fall within the range of observation. There are several other weak bands recorded, but these are all on the high wave-length side of 600 Å. It is quite probable, however, that there is no molecular $1\sigma^1\Sigma$ term, since this would involve the presence of three $1s$ electrons in the molecule. It is desirable that further work should be carried out in this region, using conditions specially favourable for the production of the band spectrum, together with higher resolving power.

It is evident that the infra-red spectrum of He_2 will be very complex. The strongest band should be $2\pi^3\Pi \rightarrow 2\sigma^3\Sigma$ at about $2{\cdot}047\mu$, and we should also expect to find $3\sigma^3\Sigma \rightarrow 2\pi^3\Sigma$ ($1{\cdot}05\mu$), $4\pi^3\Pi \rightarrow 3\sigma^3\Sigma$ ($1{\cdot}47\mu$), $4\sigma^3\Sigma \rightarrow 3\pi^3\Pi$ ($1{\cdot}90\mu$), $4\pi^3\Pi \rightarrow 3^3\delta$ ($2{\cdot}01$-$1{\cdot}78\mu$), $4^3\delta \rightarrow 3\pi^3\Pi$ ($1{\cdot}67$-$1{\cdot}75\mu$), higher members of these series, a set of bands involving a ϕ term, and all the corresponding ${}_p\mathrm{He}_2$ bands. They will each have an appreciable width (of the order of $0{\cdot}1\mu$) and will overlap to a considerable extent. Most of them will have no well-marked head, and intervals between successive lines will usually be well below $0{\cdot}01\mu$. The difficulties of analysis will thus be very great in this region, in fact probably insurmountable at present except in the part where photographic methods are applicable.

Some radiations presumably belonging to the He_2 spectrum have recently been reported by Takamine and Suga [43] between $\lambda\lambda$691 and 936 $m\mu$. There are various bands, mainly vibrational, to be expected in this region, but as the data are only provisional it would be premature to discuss possible identifications. It is very probable, however, that the "heads" at 912 and 920 are actually the R and P branches of the band $2\pi^3\Sigma \rightarrow 2\sigma^3\Sigma$, the origin of which should fall at λ9166 Å.

The Rotation Structure.

The bands differ greatly in the number and appearance of their branches, but the rotation structure is completely explicable on the basis of the following term scheme:—

j	a	b	a	b	a	b	a	b	a
5	o	—	o	—	o	—	o	—	o
4	—	×	—	×	—	×	—	×	—
3	o	—	o	—	o	—	o	—	o
2	—	×	—	×	—	×	—	×	—
1	o	—	o	—	o	—	o	—	—
o	—	×	—	—	—	—	—	—	—
	S	U	P		Z	XY		D	
	$\sigma\Sigma$	$\pi\Sigma$	$\pi\Pi$		$\delta\Sigma$	$\delta\Pi$		$\delta\Delta$	

The S, U and Z levels are single and the remainder double. Alternate levels of each set are completely suppressed in the manner shown. The a and b sets are quite distinct, and in fact often diverge widely from one another. It may readily be verified that $S \rightarrow U$ and $Z \rightarrow U$ bands should give P and R branches, that $P \leftarrow\rightarrow S$, $Z \rightarrow P$ and $XY \rightarrow U$ should give P, Q and R, and that $XY \rightarrow P$ and $D \rightarrow P$ should give two sets of P, Q and R. The distribution of intensity between the branches is often anomalous, as is also the course of the branches in certain cases. The discussion of these is reserved for the next section, but we may indicate here the mode of derivation of the rotation term differences.

If in a given band there are two branches derived from the same two sets of states the term differences of both are directly obtainable. Thus in the case of $\Pi \rightarrow \Sigma$ bands * the P and R branches are both derived from the states Π_b and Σ, thus :—

$$P(j) = \Pi_b(j-1) - \Sigma(j),\ R(j) = \Pi_b(j+1) - \Sigma(j).$$

Hence $$\Delta\Pi_b(j) \equiv \Pi_b(j+1) - \Pi_b(j-1) = R(j) - P(j),$$

and $$\Delta\Sigma(j) = R(j-1) - P(j+1).$$

The Q branch involves the Π_a state, thus :—

$$Q(j) = \Pi_a(j) - \Sigma(j),$$

so that the Π_a differences can only be evaluated by making use of the P and R branches also, thus :—

$$\Delta\Pi_a(j) = Q(j+1) - Q(j-1) + R(j-1) - P(j+1).$$

There are some cases in which only two branches are observed, but they involve three states instead of two, for instance in the $Z \rightarrow P$ bands, where we have

$$Q(j-1) = Z(j-1) - P_a(j-1), \text{ and } R(j) = Z(j+1) - P_b(j).$$

In order to find the Z term difference we may make use of the difference $P_b(j) - P_a(j-1)$, which is obtainable by combining the Q and R branches of the $D \rightarrow P$ bands.

Finally, there is sometimes only one branch of observable intensity, as in the band $5^1Z \rightarrow 2^1P$, where we have $R(j) = Z(j+1) - P_b(j)$. In this case $\Delta Z(j) = R(j) - R(j-2) + \{P_b(j) - P_b(j-2)\}$, and the difference in brackets is known from other bands involving these terms. This procedure is of course only applicable when one of the two term differences concerned is already known.

The rotation terms themselves are readily obtainable from the differences when the form of the term-function is known, as for example in

* Π and Σ are used here in preference to P and S in order to avoid confuson between the P level and the P branch.

the case of the S terms, where $S(j) = Bj(j+1) - \beta j^2(j+1)^2$. In most other cases it is not possible to represent the terms by a simple formula, and only an approximate value of B is obtainable. Dieke [42] has given a method of deriving the relative values of the terms, and has also discussed these in relation to the theoretical results of Hill and van Vleck.*

The Vibration Structure.

This is exceptionally simple, in that for any particular electron transition the $0 \rightarrow 0$ band is always much the strongest. Next in intensity comes the $1 \rightarrow 1$, then $0 \rightarrow 1$, $1 \rightarrow 0$, $2 \rightarrow 2$, etc.[33] This low intensity of the vibrational bands is presumably related to the low stability of the He_2 molecule, and it is worthy of note that in the $\pi^3\Pi$ sequence the vibrational bands have only been traced to the point ($n = 7$) at which the vibrational and electronic terms are approaching equality, being 1629 and 2285 respectively. For $n = 8$ they would be about 1628 and 1745.

The values of the vibrational frequency associated with the various electronic levels are given in Table II.

TABLE II.—Vibration Frequencies for ${}_0He_2$.

n.	2.	3.	4.	5.	6.	7.	8.	9.
$\sigma\Sigma$	1732	1654	1635	1632	—	—	—	—
$\pi\Pi$	1697·7	1651·2	1637·5	1632·6	1630·2	1629·2	1629†	1628†
$\delta\Sigma$	—	1549	1594	—	—	—	—	—
$\delta\Pi$	—	1569	1600	—	—	—	—	—
$\delta\Delta$	—	1636	1629‡	—	—	—	—	—

The chief feature of interest attaching to these results is the way in which they tend to a common limit (about 1628) with increasing n. In the well-developed $\sigma\Sigma$ and $\pi\Pi$ sequences this is quite evident, and the onset of a similar change is to be seen also in the other sequences. This limiting frequency is that characteristic of the He_2^+ ion. It may also be noted that whereas for the $\sigma\Sigma$, $\pi\Pi$ and $\delta\Delta$ sequences the limit is approached from above, for the $\delta\Sigma$ and $\delta\Pi$ sequences it is approached from below. This indicates that the strength of the binding decreases in the former case but increases in the latter, a difference which is no doubt connected with the uncoupling process discussed below.

Weizel [27] has estimated an upper limit for the heat of dissociation of He_2 as 19,000 cm.$^{-1}$ (55,000 cal./Mol.).

Uncoupling Phenomena.

The helium bands, and especially those associated with the "additional" electronic terms, exhibit some remarkable structural features which will now be discussed in some detail. It will be convenient to

* *Physical Rev.*, **32**, 250, 1928.
† From 40. Remainder from 27 and 32.
‡ Derived from data in ref. 31.

describe first some of the peculiarities of structure and intensity, then to examine the properties of the corresponding rotation terms, and finally to outline the theoretical explanation of the apparent anomalies observed.

(*a*) *Structure of the Bands.*—In every electronic series of bands there

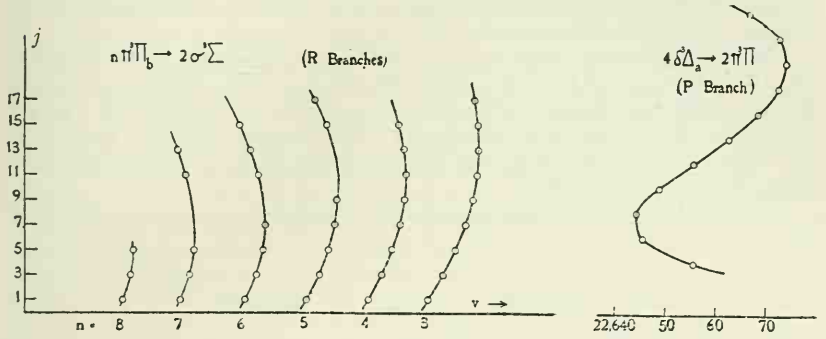

FIG. 1.

is a progressive change of structure and usually also of intensity distribution between the branches. Some illustrations of the former are given in Figs. 1 to 3.

Fig. 1 shows the progressive change in the *R* branches of the bands

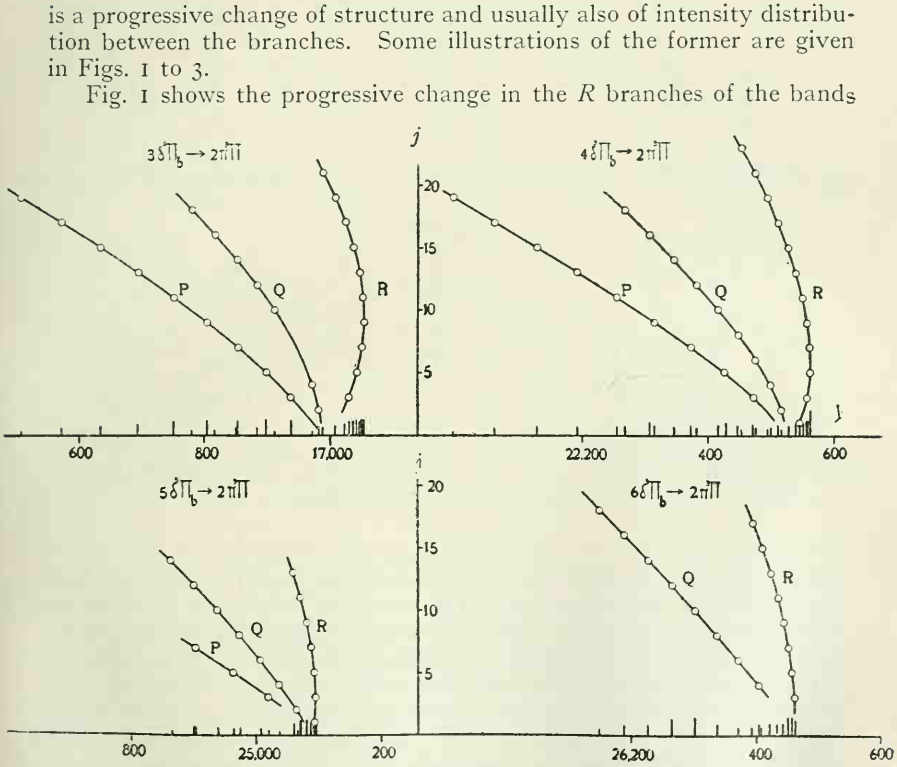

FIG. 2.

$n\pi^3\Pi \rightarrow 2\sigma^3\Sigma$ ($n = 3$ to 10). The turning point occurs earlier and earlier as n increases, that is to say, the branch is tending towards the Q form. This is due to a progressive change in the $\pi\Pi_b$ terms; the Q branches, which are derived from $\pi\Pi_a$, show practically no change.

Fig. 2 illustrates the development of the $n\delta^3\Pi_b \rightarrow 2\pi^3\Pi$ bands. The first, $n = 3$, is of normal appearance, except that the R branch turns rather quickly and the first few Q lines are abnormally weak,* but for $n = 6$ the R branch has become of Q form and the Q branch of P form, whilst the P branch has become too weak to observe. The intermediate stages are well shown for $n = 4$ and 5.

Fig. 3 shows the bands 3, 4 and 5 $\delta^3\Pi_a \rightarrow 2\pi^3\Pi$, and $3\delta^3\Sigma \rightarrow 2\pi^3\Pi$. The first is unusual in that the P branch is nearly of Q form, the Q branch nearly of R form, whilst the R branch is of "double R" form. These peculiarities tend to disappear with increasing n, and for $n = 5$ the appearance of the branches is practically normal, except that the P branch is very weak.

The $n\delta^3\Sigma \rightarrow 2\pi^3\Pi$ bands present some striking anomalies. They all

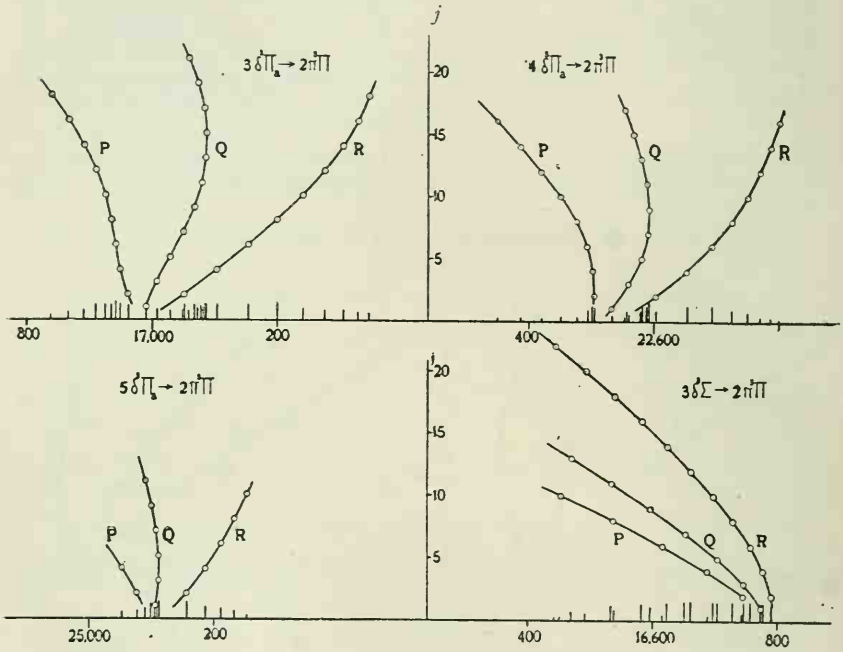

Fig. 3.

consist of strong Q and R branches, and a very weak P branch has been found [20] in the first member ($n = 3$) but in no other. In this case the R branch has a form something between a Q and a P branch, and lies entirely on the low frequency side of the origin. The Q branch is of P form. In both cases the line intervals follow an unusual course for low j values, indicating a marked departure from the parabolic formula which fits most of the other rotation terms in this spectrum. This particular anomaly tends to disappear with increasing n, and eventually, for $n = 6$, the R branch assumes a quite normal P form. The Q branch is relatively weaker for $n = 4$ than for $n = 3$, and still weaker for $n = 5$ and 6.

The $\delta\Delta \rightarrow \pi\Pi$ bands are not yet so well observed as $\delta\Sigma$ and $\delta\Pi \rightarrow \pi\Pi$,

* In consequence the Q branch was missed in the first analysis of this band.[18]

but they show some interesting features. So far as can be judged from the available data they exhibit a tendency to develop in the opposite manner to the $\delta\Pi_b \rightarrow \pi\Pi$ series. Thus, for example, whilst $3\delta^3\Delta_b \rightarrow 2\pi^3\Pi$ is normal in appearance, in $5\delta^3\Delta_b \rightarrow 2\pi^3\Pi$ the P branch has assumed a Q form, the Q branch an R form and the R branch a " double R " form. There are some striking peculiarities also in some of the branches. Thus in $3\delta^3\Delta_b \rightarrow 2\pi^3\Pi$ the Q branch begins in the ordinary way, opening out from a head near the origin, but for higher j values the spacing decreases again. The Q branches of $4\delta^3\Delta_a \rightarrow 2\pi^3\Pi$, $4\delta^3\Delta_b \rightarrow 2\pi^3\Pi$ and $3\delta^1\Delta_b \rightarrow 2\pi^1\Pi$ behave in a similar way. The P branch of $4\delta^3\Delta_a \rightarrow 2\pi^3\Pi$ is still more remarkable in possessing two heads, one at $j = 8$ and the other at $j = 20$. That is to say, it starts off from the origin like an ordinary P branch, towards the low frequency side, reaches a head, turns back, crosses the origin, reaches a second head on the high frequency side and turns back again. It is shown on the right-hand side of Fig. 1.

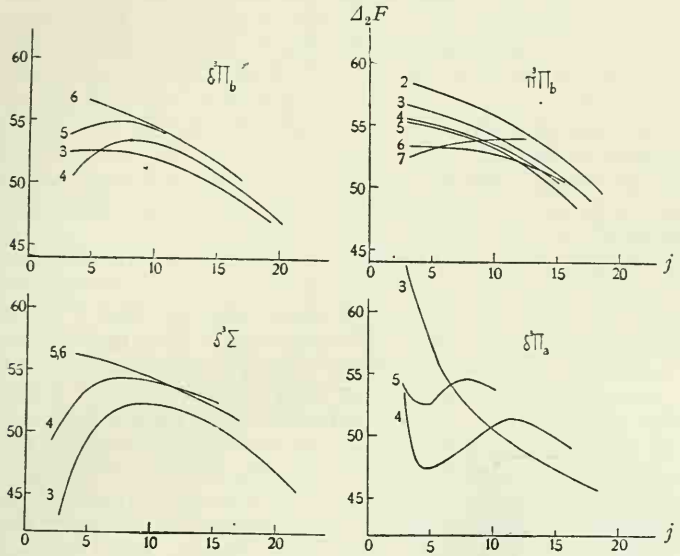

FIG. 4.—Second differences (Δ_2F) of rotation terms.

(*b*) *The Second Differences of the Rotation Terms.*—The peculiarities of structure referred to above must originate in the initial terms, since the final terms $2\sigma\Sigma$ and $2\pi\Pi$ are quite normal. In most cases the terms themselves are not readily obtainable, but a study of their second differences yields some useful information concerning them. In the case of the " normal " type of rotation term the second differences are an approximately parabolic function of j, tending to the value $8B$ for the lowest j value which can exist (0 for Σ, 1 for Π, 2 for Δ levels). This applies to all the $\sigma\Sigma$ and $\pi\Pi_a$ terms and to the first few $\pi\Pi_b$ terms, as will be seen from Fig. 4, but to hardly any others. For example, the early (*i.e.*, low n and j) $\delta\Pi_b$ and $\delta\Sigma$ differences fall considerably below the normal values, whilst the corresponding $\delta\Delta$ and $\delta\Pi_a$ values are abnormally high. Weizel [25] has proposed an explanation of these deviations which is based upon an interaction between the molecular rotation and the electronic angular momentum, l. The latter is in the first

instance coupled to the inter-nuclear axis, around which it executes a regular precession, but this may be disturbed by the influence of rotation in such a manner at to develop a component ρ parallel to the rotation axis. This may be either positive or negative, and is responsible for the differentiation of the a and b sub-states. Weizel showed that in consequence of this the second differences for low j should be decreased below the normal when ρ is positive, and increased when it is negative. This behaviour is shown by the curves for $3\delta\Pi_a$ (very pronounced) and $3\delta\Pi_b$ (perceptibly), and this was part of the evidence on which Weizel interpreted them as b and a sub-states of the same electronic level. The $\pi\Pi_b$ differences are at first normal, but with increasing n, develop an anomaly indicating a positive ρ.

It is noteworthy that with increasing n and j the disturbances tend to disappear and in nearly all cases the curves approximate to the same slope. This is well shown by the $\delta\Pi_b$ and $\delta\Sigma$ levels. In the latter case, for instance, the anomaly is very marked for $n = 3$, less so for $n = 4$, and practically non-existent for $n = 5$ and 6. In the former case the anomaly develops between $n = 3$ and $n = 4$, decreases for $n = 5$, and is hardly perceptible for $n = 6$.* The $\pi\Pi_a$ curves are rather different from the others in that $n = 3$ gives very high values and $n = 4$ and 5 are very disturbed near the origin, so much so in fact that their genuineness would have been very doubtful had they not resembled one another so closely. All identifications of lines were made before these curves were plotted. The $\delta\Delta$ series are too incompletely observed to permit of the changes with n being followed.

(*c*) *The Rotation Term Differences.*—The second differences have been used mainly for establishing deviations from the normal rotation term function, but they also provide evidence that for high j values these deviations tend to disappear. This behaviour is more readily interpreted from a study of the first differences, which will now be considered therefore. A complete table of these has been given elsewhere,[36] but the data in Table III. below will suffice to illustrate their general behaviour.
In each sequence only the first and last sets of ${}_o\mathrm{He}_2$ differences are given. If the disturbances already noted in the low j region are disregarded for the moment, some very simple regularities emerge. In every sequence as n increases the differences tend to the same set of values ; this applies also to the $\sigma\Sigma$ and to both sets of $\pi\Pi$ differences. These limiting values are given at the foot of the table. The ${}_p\mathrm{He}_2$ differences, although less completely known, behave in exactly the same way and tend to the same limiting values. These must therefore be the differences for the He_2^+ ion. There is thus an exact analogy with the vibration frequencies, but in this case further information is obtainable by noting the j values which correspond to the limiting differences. As indicated by the dotted lines in the table, these differ by unity for each successive electronic level. That is to say, the effective j values are different, being $(j - 2)$, $(j - 1)$, j, $(j + 1)$ and $(j + 2)$, for $\delta\Sigma$, $\delta\Pi_b$, $\delta\Pi_a$, $\delta\Delta_b$ and $\delta\Delta_a$ respectively. This is evidently to be interpreted as due to the development of ρ to the point where it becomes a true quantum number having the respective values 2, 1, 0, — 1, — 2. In other words, the coupling of l to the nuclear axis is replaced by a coupling to the rotation axis, and a ρ-classification must therefore be substituted for the previous σ-classification.

* In the figure the perturbations have been smoothed out. The curves for $n = 5$ and 6 differ so little that it is permissible to combine them.

TABLE III.—Rotation Term Differences for $_0He_2$, $l = 2$.

ρ.	Term.	j 2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.
2	$3\delta\Sigma$	45·08		89·03		138·49		190·19		242·44		294·61		346·23		396·85		446·25		494·09
	$6\delta\Sigma$			71·40	†	126·02		183·33		238·90		292·90		346·40		398·39				
1	$3\delta\Pi_b$		92·11		144·73		197·25		249·70		301 69		352·91		403·42		452·49			
	$6\delta\Pi_b$			126·95		183·15		238·85		293·22		346·82		399·27		450·15				
0	$3\delta\Pi_a$	89·52?		153·16		210·42		263·90		315·26		365·21		413·70		461·15				
	$5\delta\Pi_a$	78·59		132·25		184·88		239·33		293·55		346·95		399·03		450·05				
— 1	$3\delta\Delta_b$		105·42		164·70		223·01		279·97		335·59		389·60		441·66					
	$5\delta\Delta_b$		122·82		180·87		237·29		292·10		345·86		398·13		449·28					
— 2	$3\delta\Delta_a$			135·65		195·58		254·73		312·81		369·44		424·07						
	$5\delta\Delta_a$			175·84		235·28		290·92		344·97		396·86		447·56		498·40				
	He_2^+	70·9		127·5		183·4		239·0		293·5		347·0		399		450				

† Indicates perturbation.

In the case of the π-complex ($l = 1$) similar tendencies exist, although they are much less marked. The $\pi\Pi_b$ and $\pi\Pi_a$ levels resemble $\delta\Pi_b$ and $\delta\Pi_a$ and the $\pi\Sigma$ appears to correspond to $\delta\Delta_b$, although only one member of the sequence is known as yet. The uncoupling process is only just beginning, but there is little doubt that the ultimate ρ values would be 1, 0 and -1 respectively.* The $\sigma\Sigma$ levels show a slight decrease and require $\rho = 0$ as would be expected.

The correlation of the two classifications is set out in Fig. 5, which is equivalent to tables given by Dieke.[41]

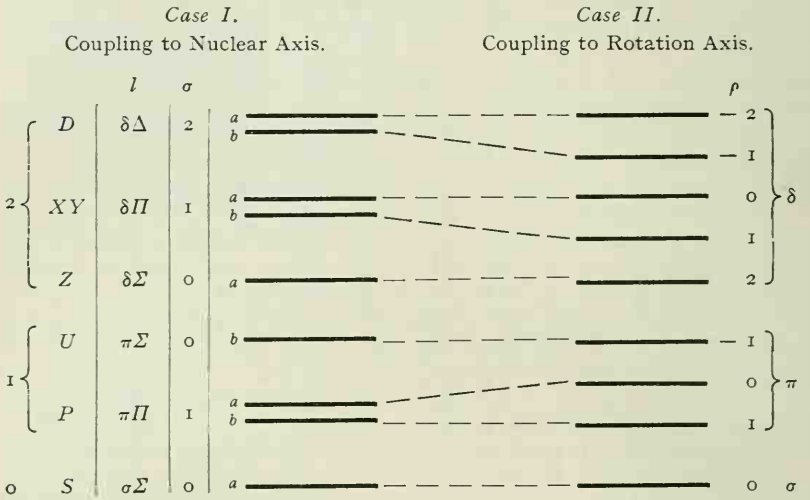

FIG. 5.—Correlation of Term Types in He_2.

This is intended to show the relative order of the terms, but not their actual positions to scale. Weizel has given reasons for thinking that the electronic quantum number of the $\pi\Sigma$ is 3 and not 2 as assumed here, but the theoretical considerations he advances would not seem to be very securely established for molecules. It should be remarked, however, that on the view adopted here the π-complex is inverted and l has a negative coupling coefficient.[41]

Some of the peculiarities of intensity may be accounted for on the same basis, if we assume that in addition to the rule $\Delta j = 0, \pm 1$ we also have $\Delta(j - \rho) = 0, \pm 1$. Considering the transition $6\delta\Pi_b \rightarrow 2\pi\Pi$ for example, where $\rho = 1$ and 0 (very nearly) respectively, the PQR branches will arise from the $(j - \rho)$ transitions $(j - 2)$, $(j - 1)$, $j \rightarrow j$ respectively. The first of these is prohibited, which accounts for the absence of a P branch, and the other two will give branches of P and Q form although actually Q and R. We may account on similar lines for the fading out of branches in other cases, notably for the $\delta\Sigma$ levels. A more detailed explanation of intensity distribution can be obtained, according to Dieke,[41] by applying the formulæ of Hill and van Vleck.† In this connection the most striking anomaly occurs in the $\delta\Sigma \rightarrow \pi\Pi$ bands, which tend to reduce to an R branch of P form, which for $n = 3$

* Dieke[29] assigned $\rho = -1$ to $\pi\Pi_b$ and $+1$ to $\pi\Sigma$, but these are interchanged, as above, in his last paper.[41]

† *Loc. cit.*

shows a pronounced disturbance for small j, but is normal throughout for $n = 6$. In the latter case the change-over in coupling is evidently complete, whilst in the former it is in progress, ρ increasing with j. The $\delta\Pi_b \rightarrow \pi\Pi$ series gives evidence of a more gradual uncoupling, just beginning for $n = 3$ and progressing practically to completion for $n = 6$. In $3\delta\Pi_b \rightarrow 2\pi\Pi$ Case I. applies for low j values, so that the transition must be classified as of $\Pi \rightarrow \Pi$ type, in which Q branches do not occur. For higher j values the differences indicate that a ρ is developing, and Case II. is approached, for which a Q branch is to be expected. The abnormal initial weakness of the Q branch of this band, followed by a rise of intensity for higher j values, is thus accounted for (Dieke). The $\delta\Pi_a \rightarrow \pi\Pi$ series stand somewhat apart from the rest, in that marked anomalies occur in the early members, although ultimately $\rho = 0$.

Dieke has recently succeeded in showing [41] that all the chief phenomena associated with the uncoupling process may be accounted for on the basis of Hill and van Vleck's formulæ. It is not possible to obtain a complete quantitative explanation, that is to say, to calculate the actual rotation terms in all cases, but a very successful qualitative interpretation of the above anomalies is given. The investigation also provided approximate numerical values for the degree of coupling and for the rotational term constant B, previous estimates of which are now seen to require correction in some cases. Thus, for example, the value for $3\delta\Delta$, which was previously abnormally high (7·6), and that for $3\delta\Pi_b$, which was abnormally low (6·6), now fall satisfactorily into line with the rest.

The values at present available (Dieke [41]) are given in Table IV. below. The values marked δ_a and δ_b have been derived respectively from the three a terms and the two b terms of the δ (*i.e.*, $l = 2$) complex.

TABLE IV.—Values of the Rotational Term Constant B for $_0He_2$.

n.	2.	3.	4.	5.	6.	7.	8.	9.
$\sigma\Sigma$	7·589	7·227	7·149	7·117	7·109	—	—	—
$\pi\Sigma$	6·852	—	—	—	—	—	—	—
$\pi\Pi$	7·336	7·173	7·128	7·113	7·108	7·105	7·103	7·101
δ_a	—	7·034	7·067	7·092	—	—	—	—
δ_b	—	7·072	7·088	—	—	—	—	—

With increasing n the values tend to a limit about 7·10, $\sigma\Sigma$ and $\pi\Pi$ approaching from above and δ from below. Precisely the converse holds for the electronic effective quantum numbers,* and if this is true in general the low B value for $\pi\Sigma$ indicates a high value for the effective quantum number and thus supports the interpretation of $\pi\Sigma$ ($n^* = 2{\cdot}16$) as a 2 quantum level. The limiting value 7·10 leads to a moment of inertia of the He_2^+ ion of $3{\cdot}90 \times 10^{-40}$ gm.-cm.^{2} and a nuclear separation of 1·087 Å.

* See Table I.

Perturbations and Zeeman Effect.

Up to the present the existence of ten well-marked perturbations has been established, all of them in the ${}_0He_2$ system.[36] It is possible that there are a few more, but the wide spacing of the lines and the frequent deviations from the Kratzer formula makes them difficult to identify with certainty unless they are of considerable magnitude. Of these ten, six are evidently related in pairs, as pointed out by Dieke,[28, 42], namely $4\sigma\Sigma$ (17) and $4\delta\Sigma$ (17), $5\sigma\Sigma$ (9) and $5\delta\Sigma$ (9), $6\sigma\Sigma$ (5) and $6\delta\Sigma$ (5).* Kronig's theory † of perturbations in band spectra indicates that they probably originate in the close approach of the pairs of terms in question, and the fact that the displacements in each pair are in opposite directions supports this view. This leaves unexplained the perturbations of $4\pi\Pi_b$ (6), $5\pi\Pi_b$ (2), $4\pi\Pi_a$ (9) and $5\pi\Pi_a$ (5). It may be noted that as in every other case the j value corresponding to the perturbation decreases as n increases, but none of the term sequences hitherto recognised would seem to be responsible for any of these perturbations. As they do not fulfil the conditions which render interaction possible this provides further support for the theory. It may be that the interacting terms belong to the $\pi\Sigma$ or ϕ sequences, of which only $2\pi\Sigma$ is known.

Curtis and Jevons[19] have investigated the Zeeman effect on the $\pi\Pi \longleftrightarrow \sigma\Sigma$ type bands in fields up to 20,000 gauss. The results were qualitative only, as resolution into components was not effected, but taken in conjunction with further unpublished data they show that magnetic behaviour of the term is intimately connected with its coupling characteristic.

I am indebted to the Department of Scientific and Industrial Research for the means of obtaining assistance in the preparation of this paper.

Summary.

An account is given of the present position with regard to this spectrum, the analysis of which is nearly complete in the visible and near ultra-violet regions. Two systems exist, triplet and singlet, the former being considerably the stronger ; otherwise they are quite similar. All the six types of electronic level derived on Hund's theory from the l-values 0, 1, 2 have been identified, and in most cases at least three or four members of the sequence are known. The structure of successive bands in one sequence shows a progressive change which may be attributed to a change in the coupling of l. For low n and j values, Case I. (coupling to nuclear axis, σ classification) usually applies, and for high n and j values, Case II. (coupling to rotation axis, ρ classification). The transition from one to the other gives rise to striking anomalies of structure and intensity by consideration of which the process can be followed in some detail. The first and second differences of the rotation terms yield important evidence in this connection. The former appear to extrapolate for large n to the same set of values in every sequence. These limiting values are identical for the two systems, and must refer to the He_2+ ion. The j values associated with them differ by 0, $\pm$ 1 and $\pm$ 2 from those derived from the S sequence, and therefore give the ρ values directly. The vibration frequencies in each sequence similarly extrapolate to a common value, that of the He_2+ ion.

The values of the electronic terms and the vibration frequencies are tabulated, and also the rotation term differences for the first and last members of each sequence. The structure of a number of bands is shown graphically in order to illustrate the effects of the uncoupling process, and the second differences of the rotation terms are also plotted. A diagram is given showing the correlation between the electronic terms in Cases I. and II., and a complete bibliography is appended.

* Misprinted as $6\delta\Sigma$ (7) in ref. 36.

† *Z. Physik*, **50**, 347, 1928.

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THE DETERMINATION OF HEATS OF DISSOCIATION BY MEANS OF BAND SPECTRA.

By Professor Raymond T. Birge.

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Three years ago, Miss Sponer and I published a paper[1] entitled "The Heat of Dissociation of Non-Polar Molecules." In that paper we gave a method for calculating heats of dissociation (D) from band spectra, when the known energy levels ended far from the actual point of dissociation, and we applied this method to a determination of D for O_2, O_2^+, N_2, N_2^+, CO, CO^+, and NO. The present communication is, in

[1] R. T. Birge and H. Sponer, *Physical Rev.*, **28**, 259, 1926.

one sense, a revised edition of this former paper, written in the light of information, both experimental and theoretical, which has accumulated since that time. The essential new information I desire to present is a method for plotting frequency of vibration, leading, I believe, to much more trustworthy values of the heats of dissociation. This work was started only two months ago, having unfortunately been greatly delayed by my long paper on the General Physical Constants. Since then it has been interrupted by the work on Isotopes, described in another paper. The results already obtained seem, however, of sufficient interest to be worthy of presentation. In fact, if even these preliminary results are given in any detail, the present paper would be several times the length requested for this Symposium.

The essential goal of experimental spectroscopy, at the present time, is the determination of the energy levels of atoms and molecules, by means of the now famous combination principle. The interpretation of these energy levels is partly a matter of theory and partly of experiment. Fortunately, there has been in the case of molecules a most satisfactory agreement between theory and experiment, in regard to such interpretations. One of the most striking facts concerning sets of energy levels is that they are often observed to approach a point of confluence, that is, the separation of successive levels approaches zero. It has been experimentally proved, in the case of atoms, that an electron is separated from the atom, at the critical energy corresponding to the point of confluence. Similar sets of energy levels, called electronic energy levels, have been observed for a few molecules, notably H_2 and He_2, and the interpretation is the same as in the case of atoms. A much more prevalent case, however, is that of sets of *vibrational* energy levels. Although the experimental work on this point is far less extensive, it can safely be stated that dissociation occurs at the point of confluence of such molecular energy levels—that is, one portion of the molecule, normally one atom, is separated from the remaining portion. The corresponding critical energy is, by definition, the heat of dissociation (D) *for the process involved.* If, then, one can follow such a set of molecular energy levels up to, or almost up to, the point of confluence, the value of D becomes definitely known. The difficulty here lies solely in deciding just what is the "process involved." It is now quite certain that molecules in most excited electronic states, and sometimes even in the normal state, dissociate into products which include at least one *excited* atom. To calculate the ordinary heat of dissociation, as defined by the chemist, it is therefore necessary to know just what are the products of dissociation, especially as regards their residual energy content.

A second problem arises when it is possible, with the available experimental material, to follow a set of vibrational energy levels only a small fraction of the distance to dissociation. The proper extrapolation of such an incomplete set of levels, to obtain the energy at which dissociation occurs, is the main subject of this paper. Experimental material for many diatomic molecules indicates that the vibrational energy can be represented, to a first approximation, by

$$E_n = \omega_0 n - \omega_0 x n^2 \quad . \quad . \quad . \quad . \quad (1)$$

Here, as usual, we have divided through by hc, and the energy is thus expressed in cm.$^{-1}$ units. The separation of successive energy levels is then given by

$$\omega_n = \frac{dE_n}{dn} = \omega_0 - 2\omega_0 x n \quad . \quad . \quad . \quad . \quad (2)$$

Bohr's original correspondence principle interprets $\frac{dE_n}{dn}$ as some average frequency for two adjacent levels, and it is therefore denoted ω_n. Numerically it represents the separation of two such levels, ΔE_n and can be evaluated directly from the data. A plot of ω_n as a $f(n)$ shows [2] that it is often linear, in agreement with equation (2). In such cases Birge and Sponer made a simple linear extrapolation to $\omega_n = 0$, denoting by n_0 the corresponding value of n. Then

$$D = \int_0^{n_0} \omega_n dn \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Throughout this paper the nomenclature of the *old* mechanics is used. Hence n has integral values for the observed energy levels and half integral values for the observed values of ω_n.

In many other cases, however, ω_n decreases with n *more* rapidly than the linear relation. Such ω_n graphs are said to have *negative* curvature. In rare cases, notably in the case of the " B " level of H_2, the ω_n graph exhibits a *positive* curvature. In the case of the main absorption band systems of O_2, I_2, Br_2, Cl_2, and ICl, it is possible to follow the ω_n graph of the upper electronic level almost to the point of confluence. In *every* case the graph has the following standard form.[3] For small values of n it has a negative curvature. For higher values of n this changes rather suddenly into a *positive* curvature which, as far as can be detected, is retained almost to the point of confluence. The work which I have done recently, some of which is being presented here, indicates that this is indeed a standard form. An ω_n graph beginning with a negative curvature ends normally with a positive curvature. Occasionally it seems to end with zero curvature. On the other hand, if the ω_n curve starts with strictly zero curvature, it seems to continue with zero curvature. In other words, the ω_n graph is linear throughout its extent. This conclusion, if correct, justifies the linear extrapolation employed by Birge and Sponer. It is, however, essential that the ω_n graph be known over a sufficient interval of n values to decide whether it is truly linear. A very slight (undetected) negative curvature can produce quite an error in a long assumed linear extrapolation. It would appear, at the present time, that the most important values of D given by Birge and Sponer are incorrect, the error arising primarily from a misinterpretation of the products of dissociation, and secondarily from insufficient data.

In the present work I first attempted to get an analytic expression for $\omega_n = f(n)$, in the case of O_2, I_2, etc., where as just noted, the entire ω_n graph is known. Mr. C. A. Pulskamp has kindly assisted me in these calculations. We tried a polynomial of the fourth degree, thus containing five adjustable constants, and got a least squares solution, using the rapid method devised by Birge and Shea [4] Even with a curve of this complexity, it was possible in *no* case to get a satisfactory fit. The *Obs-Calc* values were such that an extrapolation of even a single unit in n, at either end of the curve, was entirely untrustworthy. The ω_n curve

[2] See Birge and Sponer, *loc. cit.*, Fig. 4, or Fig. 12, p. 132 of report on " Molecular Spectra in Gases " for many such $\omega_n : n$ graphs.

[3] See graph 20 of reference (2) for the O_2 ω_n curve.

[4] R. T. Birge and J. D. Shea, " A Rapid Method for Calculating the Least Squares Solution of a Polynomial of any Degree," *Univ. Calif. Publ. Math.*, **2**, 67-118, 1927.

evidently has a peculiar shape, making it unsuitable for representation by the usual empirical formula.

I then tried the following procedure. Instead of plotting the frequency of vibration ω_n against the vibrational quantum number n, I plotted it against the *energy* of vibration E_{ω_n} $(= \Sigma\omega_n)$. As had been anticipated, this caused the disappearance of the point of inflection, and gave a smooth graph which may be illustrated by the upper " B " level of O_2. In Fig. 1, plotted partly from new experimental data obtained by C. A. Pulskamp, the usual $n : \omega_n$ curve is labelled (a), while the new $E_\omega : \omega_n$

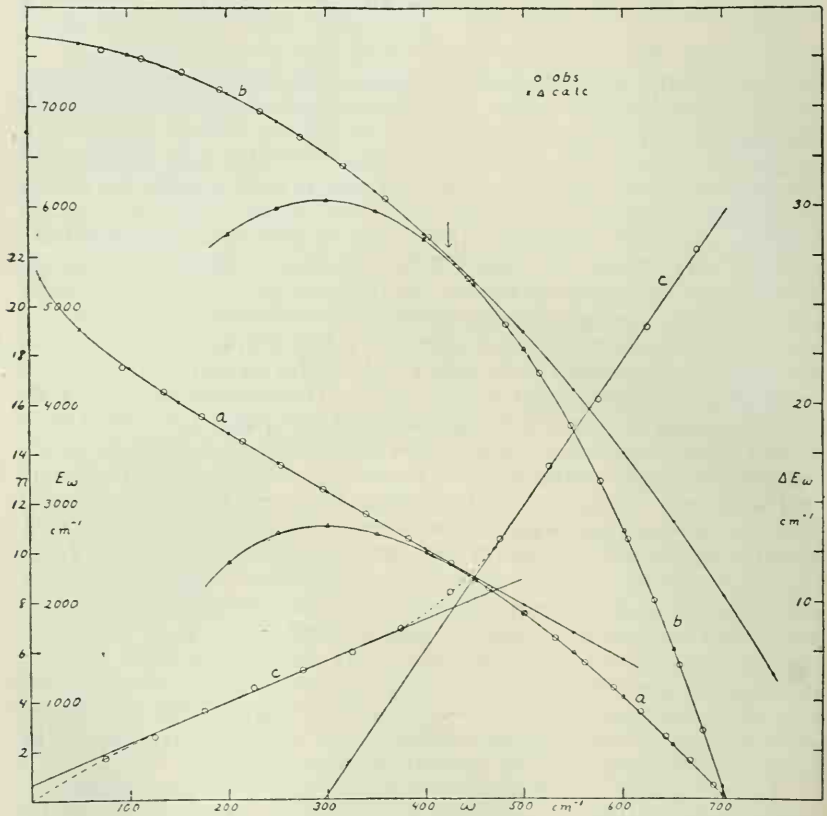

FIG. 1.—Upper " B " level of O_2. (a) $n : \omega_n$ graph, with calculated extrapolations. (b) $E_\omega : \omega_n$ graph, with calculated extrapolations. (c) $\Delta E_\omega : \omega_n$ graph.

curve is labelled (b). (For convenience ω_n is hereafter denoted ω, and E_{ω_n} is denoted E_ω.) Graph (b) obviously looks like a parabola. If it is, the first differences (ΔE_ω) should be linear in ω. Curve (c), representing these differences, gives the surprising result of *two intersecting* straight lines, showing that E_ω is indeed parabolic, but consists of *two* parabolas ! *One* of these parabolas covers that range of ω_n over which the $\omega_n : n$ curve has a *negative* curvature. The *other* parabola covers that range over which it has a *positive* curvature. The previous failure to fit the entire $\omega_n : n$ curve is now explained. It obviously takes two different functions to represent this curve, the point of inflection being actually a

point of discontinuity. It seems to me that this is a very significant conclusion. On curve (*b*), Fig. 1, only the two calculated parabolas for E_ω are shown. The discontinuity is very sharp, occurring between two adjacent vibrational energy levels, as marked by the arrow. It would appear that at this point some rearrangement of the molecular structure occurs. The data now gathered indicate that this phenomenon regularly occurs, in the process of dissociation by adiabatic increase of vibrational energy. Only in the case of linear $\omega_n : n$ curves does the discontinuity drop to zero.

The analytic relations between curves (*a*), (*b*) and (*c*) of Fig. 1 are very simple. If

$$E_\omega = a + b\omega + c\omega^2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

so that

$$\Delta E_\omega = \frac{dE}{d\omega} = b + 2c\omega \quad . \quad . \quad . \quad . \quad . \quad (5)$$

then

$$n = b \ln \omega + 2c\omega + d \quad . \quad . \quad . \quad . \quad (6)$$

$$= 2{\cdot}30258\, b \log_{10} \omega + 2c\omega + d \; . \quad . \quad . \quad (6')$$

If $b = 0$, the $E_\omega : \omega$ curve has its vertex at $\omega = 0$, and the $\omega : n$ curve becomes linear. Unfortunately, equation (6) cannot be solved explicitly for ω, and therefore the value of ω, for a given value of n, must be found by successive approximations, or other indirect methods. The relations between curves (*a*), (*b*) and (*c*) may then be stated as follows. If the $\omega_n : n$ curve has a *negative* curvature, the vertex of the $E_\omega : \omega$ parabola occurs at a positive value of ω, and the linear $\Delta E : \omega$ graph cuts the abscissa (ω) axis at this same positive value of ω. If the $\omega_n : n$ curve has a *positive* curvature, the corresponding critical value of ω is negative. Finally, if the $\omega_n : n$ curve is *linear*, the linear $\Delta E : \omega$ curve passes through the origin. This last criterion, in terms of actual numerical data, is a very sensitive test of the linearity of the original $\omega_n : n$ graph.

It should be noted that a negative curvature of ω_n corresponds to a negative value of b, in equation (6). Hence $n = -\infty$ for $\omega_n = 0$. This is, of course, physically impossible, and means that the negative curvature *must* change to positive, or at least to zero curvature, before ω_n becomes zero. On the other hand, in the case of positive curvature, b is positive, and $n = +\infty$ for $\omega_n = 0$. It is rather difficult to judge, whether equations (4), (5) and (6) are really followed to the point $\omega_n = 0$. I think it more likely that the ΔE_ω curve dips into the origin, at very small values of ω, thus giving a finite n for $\omega_n = 0$. (See broken extrapolation of curve (*c*), Fig. 1.) This agrees with Kratzer's theoretical result [5] in the case of atomic binding. On the other hand, the very accurate chemical value of the heat of dissociation of I_2, deduced by Gibson and Heitler [6] from the data of Starck and Bodenstein, requires that the ΔE curve continue linear to $\omega = 0$, and thus requires an infinite n for $\omega = 0$. This point requires further investigation.

In a brief paper like this, it is not possible to describe in detail how the data should be handled in plotting the various curves just discussed, and in obtaining the analytic formulation. I must content myself with a brief summary of the results. For the upper level of O_2 and I_2 the

[5] A. Kratzer, *Z. Physik*, **26**, 40, 1925.
[6] G. E. Gibson and W. Heitler, *Z. Physik*, **49**, 465, 1928.

"break" in the E_ω curve comes at just about 68 per cent. of the dissociation energy. It probably comes at about the same point in Br_2 and Cl_2, but because of the uncertainty as to the true values of n', this cannot be decided. The 68 per cent. is, however, not a general rule. In the case of the normal level of H_2, the known E_ω curve extends to 91 per cent. of the most probable value of D, with no sign of a break. The ΔE_ω

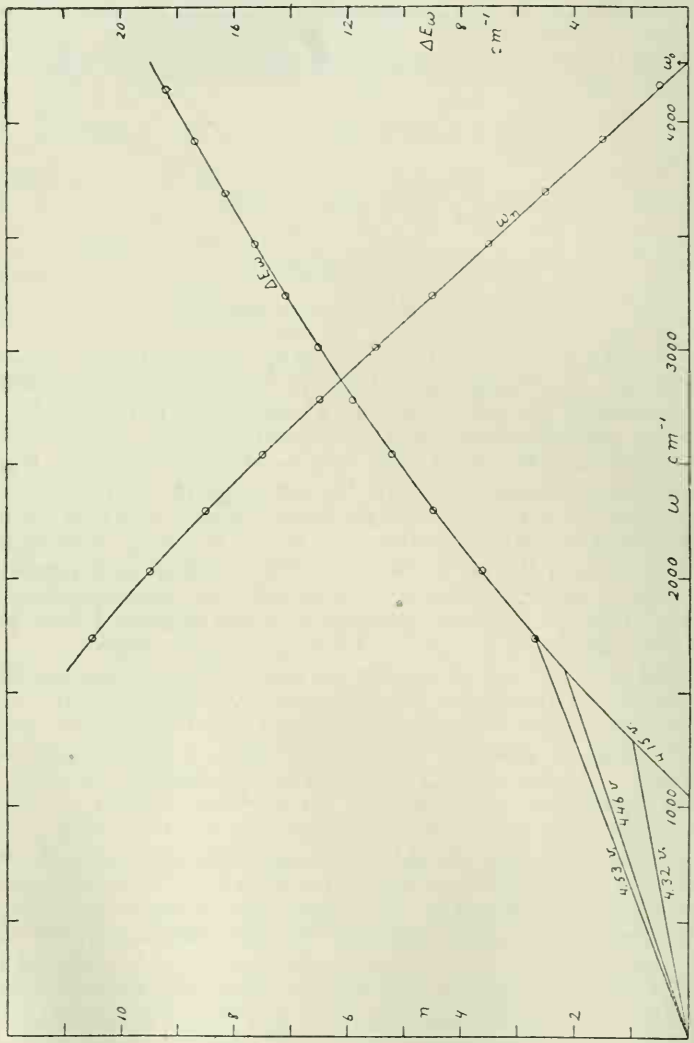

FIG. 2.—Normal level of H_2. $n : \omega_n$ and $\Delta E_\omega : \omega_n$ graphs, with possible extrapolations and resulting heats of dissociation.

curve, for this case, is shown in Fig. 2. The experimental data are quite accurate, and as shown, the ΔE_ω graph has a slight curvature, showing that equations (4), (5) and (6) need not be strictly the correct form. The "B" level of H_2, to be discussed presently, gives an even more unusual ΔE graph. The H_2 molecule seems exceptional in all ways.

If the ΔE curve of Fig. 2 is smoothly extrapolated, the resulting value of D is 4·15 volts, as noted on the graph. However, we know that

such a ΔE graph represents a possible physical condition only when it passes *through* the origin, or slightly *above* the origin. The most probable value of D, according to Richardson and Davidson[7] is 4·46 volts. Because of improved data, this is more trustworthy than the earlier value of 4·42 obtained in the same way by the writer.[8] Fig. 2 shows a ΔE_ω curve passing through the origin and so drawn as to give $D = 4{\cdot}46$ volts.[9] It is, I think, essentially the most probable extrapolation. If the " break " comes just at the end of the observed points, the value of D is 4·53 volts, as shown in Fig. 2. This is roughly a maximum value.

Passing now to the " B " level of H_2, we find the peculiar ΔE_ω curve pictured in Fig. 3. It starts out as a line pointing far *above* the origin, but quickly swings around until it points *just above* the origin. This means that the $\omega_n : n$ curve has a pronounced *positive* curvature for low values of n, but quickly becomes almost linear. The data are due to Richardson and Davidson,[10] and are quite accurate. If the observed end of the ΔE_ω graph is connected linearly with the origin, the resulting value of D is 3·36 volts. Now, if the products of dissociation from this level are one normal and one 10·15 volt excited H atom, and if the normal D for H_2 is 4·46 volts, then D^x for this " B " level should be 3·48 volts. An extrapolation of the ΔE_ω curve gently rounding to the origin will give just this value, as noted in Fig. 3. Pauling[11] has suggested that this " B " level represents ionic binding, with the ions H^+ and H^- as the products of dissociation. Recent theoretical work of Kemble and Zener[12] indicates that the binding is indeed ionic, but that the products of dissociation are neutral atoms. The data of Fig. 3 agree exactly with this last conclusion. I have drawn an extrapolation of ΔE_ω such that the area under it is 6·81 volts, the value of D for dissociation into ions, provided the electron affinity of the H atom is zero. It is obvious that the initial portion of the ΔE_ω curve, if extrapolated, might easily give such a value of D. It is equally obvious that the real curve indicates a *transition from ionic to atomic binding*, as characterised by the change to a straight line pointing toward the origin. This seems very convincing evidence on this much debated matter.

It is difficult to decide, at the present time, on the most probable value of D for N_2. This constant may be determined indirectly[13] from the value of D^x for the excited electronic level of N_2^+. The ΔE_ω graph for this level, using the data of Herzberg,[14] is beautifully linear for the higher values of ω, indicating a negative $\omega_n : n$ curve of the expected form. The ΔE_ω graph then changes *gradually* into another linear curve pointing to the origin. The linear extrapolation of the ΔE_ω graph gives 3·67 volts for D^x. I think this is trustworthy to about 0·1 volt. Using the relations discussed in reference 13, the resulting value of D for N_2 lies between 8·84 and 9·24 volts, corresponding to the possible range of assumed values for the ionisation potential of N_2, from 16·5 to 16·9 volts. In an entirely different way Kaplan[15] obtains $D = 9{\cdot}0$ volts.

[7] O. W. Richardson and P. M. Davidson, *Proc. Roy. Soc.*, **A123,** 466, 1929.
[8] R. T. Birge, *Nature*, **121,** 134, 1928; *Proc. Nat. Acad. Sci.*, **14,** 12, 1928.
[9] D is given by $\int_0^{\omega_0} \Delta E_\omega \cdot d\omega$.
[10] O. W. Richardson and P. M. Davidson, *Proc. Roy. Soc.*, **A123,** 54, 1929.
[11] L. Pauling, *Chem. Reviews*, **V.**, 173, 1928.
[12] E. C. Kemble and C. Zener, *Physical Rev.*, **33,** 512, 1929.
[13] See G. Herzberg, *Nature*, **122,** 505, 1928; and R. T. Birge and R. S. Mulliken, *Nature*, **122,** 842, 1928.
[14] G. Herzberg, *Ann. Physik*, **86,** 189, 1928.
[15] J. Kaplan, *Proc. Nat. Acad. Sci.*, **15,** 226, 1929.

The $\omega_n : n$ curve of the *normal* level of N_2 is *linear*, and its linear extrapolation gives 11·75 volts.[16] I believe that this extrapolation is essentially correct, and indicates that the normal level of N_2, like the normal level of N_2^+, dissociates into *one normal and one excited atom*. Theory and experiment agree on this point[17] in the case of N_2^+, but there may be theoretical difficulties in the case of neutral N_2. I hope to do much

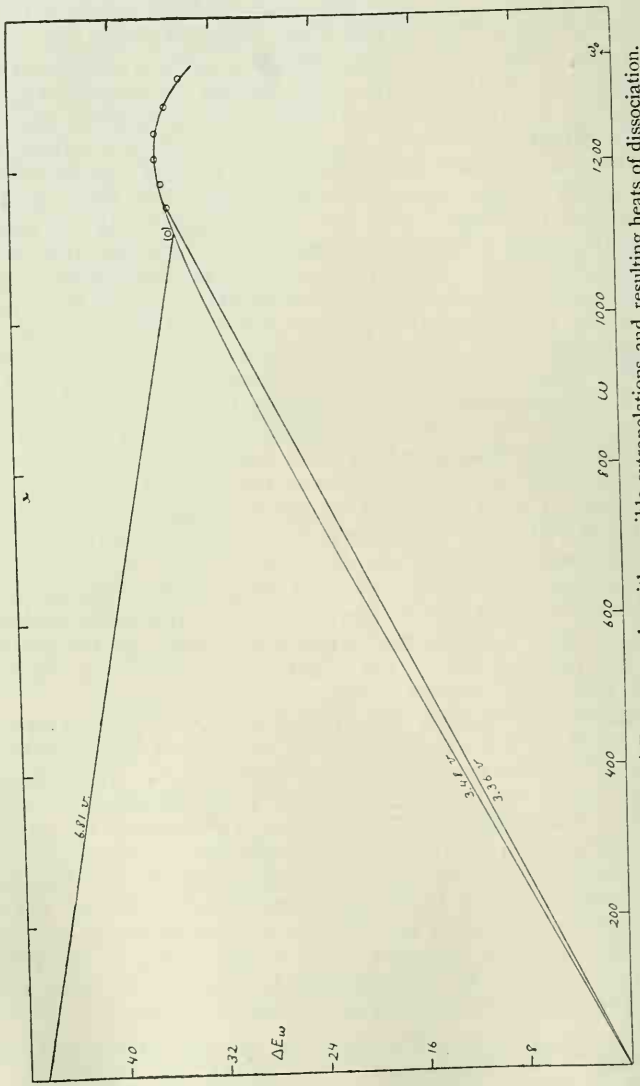

FIG. 3.—"B" level of H_2. $\Delta E_\omega : \omega_n$ graph, with possible extrapolations and resulting heats of dissociation.

further work on the various electronic levels of N_2. Such work has been started but has thus far led to no definite conclusions.

Most of the work in connection with this paper has been devoted to a study of the normal level of O_2, since this affects the calculation of the

[16] R. T. Birge and J. J. Hopfield, *Astrophys. J.*, **68**, 257, 1928. (See p. 275.)
[17] See W. Heitler and G. Herzberg, *Z. Physik*, **53**, 52, 1929.

isotope shift in O_2, as discussed in my other paper, as well as the value of D. Because of required brevity, the results are merely outlined. From the Runge bands we know[18] the vibrational levels from $n = 11$ to 17. From absorption data by Füchtbauer and Holm, we know, rather inaccurately, the values of $\omega_{1/2}$, $\omega_{7/2}$ and $\omega_{9/2}$. The resulting ω_n curve *seems* linear and leads to $D = 6{\cdot}65$ volts. On the other hand, the total energy at dissociation from the upper ("B") level of the Schumann-Runge bands is 7·05 volts. As shown by Fig. 1, this last value is accurate. Birge and Sponer based their value of D for O_2 solely on the 7·05 volt

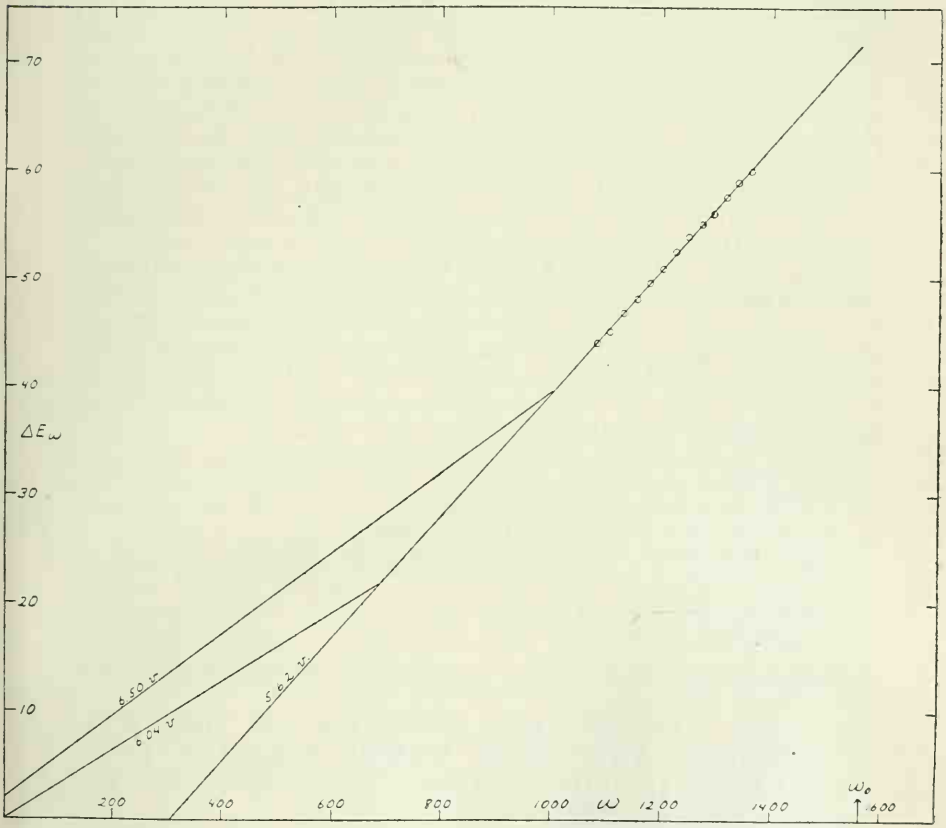

FIG. 4.—Normal level of O_2. $\Delta E_\omega : \omega_n$ graph, with possible extrapolations and resulting heats of dissociation.

result, stating that the lowest excited level in the oxygen atom was at 9·1 volts, and concluding that the products of dissociation for this B level *must* therefore be two normal atoms. In drawing this conclusion, they overlooked the important fact that Hund had *predicted* other levels (at that time unknown) of relatively low excitation potential. One of these is a ^1D level, and its position is still unknown. The other is a ^1S level, and is known, from the aurora green line, to lie 2·21 volts above the ^1D level. It is thus quite possible that dissociation from the "B" level is into one normal atom and one atom in the ^1D excited state,

[18] See reference 1 for a discussion of all previously known data.

while from the normal level dissociation into two normal atoms occurs. This assumption has now been predicted by theory.[19] The experimental proof or disproof rests on the $\omega_n : n$ curve of the normal level of O_2. *If* this has a *negative* curvature, the value of D *must be less* than 6·65 volts, and therefore *less* than the 7·05 volts given directly by level " B." I have now definitely shown that the $\omega_n : n$ curve *does have* such a negative curvature, and that D is roughly 6 volts. I think D cannot be *more* than 6·5 volts, nor *less* than 5·6 volts. In Fig. 4 are shown the ΔE_ω curve and its various extrapolations on which these conclusions are based. The data used in plotting this curve are mostly new, having been gotten from a rough analysis I have made of the Runge band wave-lengths published by Fesefeldt,[20] and more particularly from data on oxygen fluorescence recently published by Rasetti.[21] This last article allows a relatively trustworthy determination of the $\omega_n : n$ curve from $n = 8$ to 22, and as Fig. 4 shows, this curve has definitely not only negative curvature, but a curvature of the exact form demanded by equation (6). In concluding this much too brief discussion of O_2, it may be noted that the " A " level of O_2 also leads to a value of D of about 6·0 volts, while the work of Hogness and Lunn [22] gives $D = 6{\cdot}5 \pm 1$ volts.

Summarising the results, I believe that the most probable values of the heats of dissociation D are now 9·1 volts for N_2 and about 6 volts for O_2. From this it follows, by the argument used in Birge and Sponer, that the D of NO is about 6·6 volts, agreeing well with the value of 6·8 volts given by Jenkins, Barton, and Mulliken,[23] and that the D of CO is about 10·3 volts. All of these values are subject to slight revisions in the final report of this investigation.

[19] See paper by G. Herzberg, entitled " Die Dissoziationsarbeit von Sauerstoff," now in press in *Z. physik. Chem.*
[20] H. Fesefeldt, *Z. wiss. Phot.*, **25**, 33, 1927.
[21] F. Rasetti, *Proc. Nat. Acad. Sci.*, **15**, 411, 1929.
[22] T. R. Hogness and E. G. Lunn, *Physical Rev.*, **27**, 732, 1926.
[23] F. A. Jenkins, H. A. Barton, and R. S. Mulliken, *Physical Rev.*, **30**, 150, 1927.

University of California,
6th July, 1929.

ON THE ABSORPTION SPECTRA OF METHYL HALIDES AND SOME OTHER METHYL COMPOUNDS IN THE ULTRA-VIOLET AND IN THE SCHUMANN REGION.

By G. Herzberg (*Darmstadt*) and G. Scheibe (*Erlangen*),
Zweites physikalisches Institut der Universität Göttingen.

Received 9th September, 1929

In a recent paper one of us[1] has investigated the spectra of the halogen ions in solutions in the Schumann region (spectra of electron affinity). We have since measured with the same apparatus the ultra-violet absorption spectra of some methyl compounds.

The vapour streamed continuously through the absorption cell of 10 cm. length. The vapour pressure was varied between 100 and

[1] G. Scheibe, *Z. physik. Chem.*, B. **5**, 355, 1929.

1/100 mm. The evaluation of the spectrograms was carried out in the same manner as was used in the work already cited.

We wish to report here only some preliminary results obtained.[2]

1. *Methyl iodide* has a broad continuous absorption band with a maximum in the region λ2500 Å.U. Even with a large Hilger quartz spectrograph no fine structure was to be detected. We therefore believe that this band is really continuous and corresponds to a photochemical dissociation process of the molecule. The continuous absorption reaches a minimum at about λ2100 Å.U. At low pressure a discontinuous absorption of very narrow and regularly spaced bands begins at λ2010 Å.U. and extends as far as to the beginning of the secondary spectrum of hydrogen emitted by our source of light. It seems that still further in the ultra-violet a second continuous absorption begins. At somewhat higher pressures new slightly broader bands some of them having a narrow fine structure appear in the region between the narrow bands mentioned above. At the highest pressures used all light below λ2010 Å.U. is completely absorbed and at somewhat longer wavelengths two new narrow bands appear.

2. *Methyl bromide* has a quite similar absorption spectrum. Only the continuous absorption which occurs at λ2000 Å.U. in this case is still broader and the discontinuous bands beginning at λ1785 Å.U. are not by far as narrow as in methyl iodide.

3. In *methyl chloride* the maximum of the continuous absorption is displaced to λ1750 Å.U. Discontinuous absorption begins at λ1600 Å.U. and is still broader than in methyl bromide.

4. In this connection the absorption of *methyl alcohol* (CH_3OH) and *methyl cyanide* (CH_3CN) was interesting because the OH and CN groups are halogen-like. The absorption spectrum is similar to that of methyl chloride and completely continuous as far as to λ1600 Å.U.

5. Some years ago Leifson [3] found for *ethyl alcohol* a number of narrow bands in the region of λ2040 to λ1870 Å.U. As such a difference between CH_3OH (showing, as we have seen, continuous absorption only) and C_2H_5OH would be very remarkable we examined also the absorption spectrum of very thoroughly purified ethyl alcohol. We found only continuous absorption at a pressure corresponding to that of Leifson and also at other pressures. Accordingly the bands found by Leifson are to be attributed to an impurity.

The experimental results show that the first excited electron state of the methyl halides is unstable or at least much less stable than the normal state. The molecule dissociates presumably in normal CH_3 and excited I, Br or Cl in the $^2P_0$ state. If one compares the chemical and spectroscopic data, one sees that the photochemical dissociation at the point of maximum absorption takes place with great kinetic energy. We hope to discuss this point and the interpretation of the fine structure more completely in the full report of this work.

[2] The full report of this work will appear later in *Z. physik. Chem.*

[3] Leifson, *Astrophys. J.*, **63**, 1927.

RECENT WORK ON ISOTOPES IN BAND SPECTRA.

By Professor Raymond T. Birge.

Received 19th July, 1929.

I think that the Faraday Society, in a symposium on Band Spectra and Molecular Structure, is entitled to an account of the recent discovery of new isotopes from an analysis of band spectra. The present paper is thus being written, quite unexpectedly, and is to be considered merely as a preliminary statement. The detailed articles on this subject will not be ready for several months, and the final published figures and conclusions may differ slightly from those presented here.

This work on isotopes has been carried on by a group of investigators which includes H. D. Babcock and A. S. King of the physical laboratory of Mount Wilson Observatory, W. F. Giauque and H. L. Johnston of the department of Chemistry of the University of California, and the writer. The original discovery of an isotope of oxygen, of mass 18, is due to Giauque and Johnston,[1] as is the discovery of a second isotope,[2] of mass 17. In both cases they were working with data, published and unpublished, obtained by H. D. Babcock. New measurements on the oxygen isotope lines, giving the relative intensity as well as the wavelengths, and greatly extending the experimental material, have been published by Babcock.[3, 4] An error in the original theoretical calculations for oxygen was pointed out by the writer.[5] This removed an outstanding discrepancy between the calculated and observed isotope shift. In the later work on oxygen, still unpublished, the writer has been making the calculations, using data furnished by Babcock. The importance of such data, for a quantitative study of the packing effect in atomic nuclei, was first realised by Giauque, and has recently been pointed out by him.[6] The isotope of carbon, of mass 13, was first discovered by A. S. King and the writer,[7] in the Swan spectrum of C_2. Since then it has been found by the writer [8] also in the band spectra of CO and CN. Further evidence of it in CN has just been obtained by King (unpublished). This gives the status of the matter at this date (1st July, 1929). The details are as follows.

Within a year after Heurlinger's initial application of the quantum theory to band spectra, Loomis [9] and Kratzer [10] pointed out the appearance of the chlorine isotopes in the infra-red spectrum of HCl. A detailed search for isotopes in band spectra was later undertaken by R. S. Mulliken, and the results have been published in a long series of brilliant

[1] W. F. Giauque and H. L. Johnston: (*a*) *Nature*, **123**, 318, 2nd March, 1929; (*b*) *J. Amer. Chem. Soc.*, **51**, 1436, 1929.
[2] W. F. Giauque and H. L. Johnston, *Nature*, **123**, 831, 1st June, 1929.
[3] H. D. Babcock, *Proc. Nat. Acad. Sci.*, **15**, 471, 1929.
[4] H. D. Babcock, paper at Berkeley, June, 1929, meeting of Amer. Physical Soc.
[5] R. T. Birge, *Nature*, **124**, 13, 1929.
[6] W. F. Giauque, *Nature* **124**, 265, 1929.
[7] A. S. King and R. T. Birge. *Nature*, **124**, 127, 1929.
[8] R. T. Birge, *Nature*, 182, 1929.
[9] F. W. Loomis, *Nature*, **106**, 179, 1920; *Astrophys. J.*, **52**, 248, 1920.
[10] A. Kratzer, *Z. Physik*, **3**, 460, 1920; and **4**, 476, 1921.

papers.[11] It is undesirable to take up space in the present paper by any review of this previous work. I should, however, like to discuss the theory, since there are now available experimental data of such accuracy that it is necessary to carry out the theoretical calculations with unusual care. In all probability the detailed papers on this work will not be written for several months, and since other investigators will doubtless be now inspired to look for further isotopes, it seems desirable to point out, as promptly as possible, what seems to the writer the best way to make the theoretical calculations.

Two isotopes, by definition, differ in mass, but not in the net nuclear charge, nor in the number of external electrons. Hence, to a very close approximation, the electric fields of the two isotopes will be identical, and all chemical and physical properties except those depending on mass will also be identical. In particular, diatomic molecules involving isotopes, such as HCl^{35} and HCl^{37} will have the same nuclear separation, when not vibrating, and the same "Hooke's law constant" governing the vibration. The *moment of inertia* of the two will, however, be different, as will also the *frequency* of vibration, due in each case to the mass factor. The quantitative difference in any molecular constant, for the two isotope molecules, may be immediately calculated, if one knows how the various band spectra constants depend on mass. Fortunately this latter information *is* known in considerable detail.

As just noted, the electric fields of two isotope molecules should be approximately the same, but obviously they cannot be exactly the same. For a given nuclear charge, the exact energy of any electronic configuration depends on the number of external electrons present and on the quantum designation of each electron. When considered more minutely, however, the energy depends not on the net electric charge of the nucleus, but on the exact character and position of each electric constituent of the nucleus. Both the number and the position of such electric constituents must be different for two different isotopes, and hence the external electric field should be slightly different. This will cause a so-called "electronic isotope effect" in both atoms and molecules. No theory has been developed for this, in the case of either atoms or molecules, but observed shifts in atoms are of the order of magnitude of a few hundredths of a $cm.^{-1}$ unit.[12] It is probable that shifts of this order of magnitude may also be found in band spectra, and this point will be mentioned presently, in connection with the actual results.

The chief change of energy, associated with a given line of an ordinary electronic band, is due to the change in electronic configuration. This electronic change is the same for all lines of a given system of bands, and as just pointed out, should be identical, or almost identical, for two isotopes.[13] The interesting features of the band spectra of isotopes should thus appear in connection with the vibrational energy change characteristic of a given band of a system, and the rotational energy change characteristic of a given line of a band. The frequency associated with a (hypothetical) transition from one electronic configuration

[11] See Chapter V., by F. W. Loomis, of the National Research Council report on "Molecular Spectra in Gases" for an account of all isotope work in band spectra, with references, up to 1926. This reference will hereafter be denoted as "Report."

[12] For a brief summary of such work see Baly's *Spectroscopy*, Vol. II., pp. 230-3 (1927).

[13] $0{\cdot}05$ $cm.^{-1}$, for instance, represents only one part in 400,000 of the energy at $\lambda 5000$.

to another, the molecule having *zero* energy of vibration and rotation, is denoted the *origin* of the band system. According to the new wave mechanics, a molecule must always possess at least a half unit of vibrational energy. Hence the " origin " of the system is a purely calculated frequency, being related to two purely hypothetical energy states. A most direct proof, and incidentally the only proof, of the correctness of this assumption as to " zero-point " vibration, is furnished by band spectra analysis. For *if* the (0, 0) band really represented zero vibrational energy, in both initial and final states, the " origin " of this band should occur at the same frequency for each of two isotopes. Actually there is at this frequency a very definite isotope shift, of the order of magnitude of one or two cm.$^{-1}$ units for the isotopes to be discussed here. In the notation of the *old* mechanics, the true " origin " of the system is given by the hypothetical $(-1/2, -1/2)$ band. At *this* frequency the isotope shift should be zero, aside from the possible electronic shift of 0·05 cm.$^{-1}$, more or less.

The observed shift of a given spectral line now depends primarily on the *distance* of that line from the origin of the system. If all the energy change, vibrational and rotational, depended on mass in one definite way, it would be necessary merely to multiply this frequency separation by a certain mass factor, in order to get the *shift* of the corresponding lines of two isotopes. As the mass increases, *all* energy levels are more closely spaced. Hence, for the heavier isotope, all lines to the *violet* of the origin will be shifted nearer the origin and thus to *lower* frequencies. This is denoted a *negative* shift, if the heavier isotope is the less abundant, since the shift is always measured by $\nu_2 - \nu_1$, where ν_1 is a frequency associated with the more abundant isotope, and ν_2 with the less abundant. Similarly, all lines to the red of the origin will be shifted to the violet, and thus give a positive shift, in the case assumed. The important point to notice, however, is that the shift depends on the distance of a line from the origin of the system, increasing with the distance. Hence to obtain an accurate comparison between theory and experiment, one should choose lines in bands as far as possible from the origin. There is, however, one " catch " to this. In order to make such an accurate comparison, one must know exactly how the observed frequency distance is to be divided up among the different *kinds* of energy. In other words, one must know all the vibrational and rotational energy constants of the system. Now the further a line is from the origin, the more accurately these constants must be known. Thus, at the present stage of theory and experiment, it is best to work, if possible, with bands at only a moderate distance from the origin of a system (giving only a moderate change in vibrational energy), and with lines in a band at only a moderate distance from the origin of that band (giving only a moderate change in rotational energy).

Having now gotten a general idea of the nature of the isotope shift, we may pass to more detailed information. In the case of both vibrational and rotational energy, there is no one mass factor that will give the theoretical shift, although in each case there is only one important factor. Following the usual notation, let us denote by ρ the square root of the ratio of the two reduced masses μ_1 and μ_2. Then when the heavier isotope is less abundant, as is true for all cases considered here, ρ is less than unity, and $\rho^r - 1$ is negative, r being some positive integer. The *mass factor* concerned in an isotope shift is always of the form $\rho^r - 1$.

If the frequency of vibration were independent of amplitude, the

vibrational energy change would be given by $(\omega_0'n' - \omega_0''n'')$, and the corresponding isotope shift would be obtained by multiplication of this term by the mass factor $(\rho - 1)$. Here n' and n'' are the effective vibrational quantum numbers of the upper and lower levels respectively, and according to the new mechanics are *half-integers*. (More correctly, the new mechanics replaces the old integral n by $n + \frac{1}{2}$. Merely for convenience we have, however, replaced this new $n + \frac{1}{2}$ by an *effective* quantum number n, which is accordingly a half-integer and measures the amount of vibrational energy.) ω_0 is the hypothetical frequency for infinitesimal amplitude of vibration, and would be denoted by $\omega_{-1/2}$ in the old mechanics. The change of frequency of vibration with n is given, to the first approximation, by $2x\omega_0 n$, where x is a small constant. The energy of vibration is less, because of this change of frequency, by $x\omega_0 n^2$. This term is so related to mass that $\rho^2 - 1$ becomes the proper factor to use. Now, in the case of many electronic configurations, and especially in the normal configuration of a diatomic molecule, the frequency of vibration does change linearly with n, up to the highest observed values of n (15 to 20). Hence the vibrational shift is given accurately by

$$\nu_2{}^n - \nu_1{}^n = (\rho - 1)(\omega_0'n' - \omega_0''n'') - (\rho^2 - 1)(\omega_0'x'n'^2 - \omega_0''x''n''^2) \quad (1)$$

In all such equations, the constants refer to the more abundant isotope.

If the $\omega_0 xn^2$ term depended on mass in the same way as does the $\omega_0 n$ term, we could write

$$\begin{aligned} \nu_2{}^n - \nu_1{}^n &= (\rho - 1)(\omega_0'n' - \omega_0'x'n'^2 - \omega_0''n'' + \omega_0''x''n''^2) \\ &= (\rho - 1)(\nu_1{}^n) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2) \end{aligned}$$

where $\nu_1 n$ is merely the vibrational energy change, as measured by the distance of a given band origin from the origin of the band system. This last equation is equation (8), page 262 of the "Report," and has commonly been used in previous work on isotopes. Giauque and Johnston, using it, obtained 2·12 cm.$^{-1}$ for the calculated vibrational shift for the so-called (0, 0) atmospheric band [actually (1/2, 1/2) band] of oxygen. This figure is based on the assumption that the two atoms concerned have masses of exactly 16 and 18. The vibrational constants used by Giauque and Johnston contained an accidental error, as pointed out by the writer,[5] and the result, when corrected, becomes 2·053 cm.$^{-1}$. The use of equation (1) in place of equation (2) now raises this to 2·067 cm.$^{-1}$. This is *exactly* the average observed value gotten by Giauque and Johnston. But in this calculation they used also an approximate formula for rotational energy. The exact formula raises the observed 2·067 to 2·071 or possibly 2·072 cm.$^{-1}$, depending on how one weights the observations. It would appear that the observed vibrational shift is slightly larger than the calculated, and the results on the (1, 0) band, to be presented later, indicate that the discrepancy is real, and is to be attributed to the mass factor, the "18" isotope having a mass *slightly* in excess of 18.

Turning now to the rotational energy, we find that this is expressed, to a fair approximation, by the three terms

$$E_m = B_0 m^2 - \alpha n m^2 + D_0 m^4 \quad . \quad . \quad . \quad (3)$$

The main term is $B_0 m^2$ and gives the energy which the molecule would have if there were *no* change in the moment of inertia with either vibration or rotation. m is not a quantum number, but is closely related to

the rotational quantum number j, as doubtless discussed in other papers at this symposium. B_0 is not the constant found for any observed band, but is again the new mechanics calculated value, for $n = 0$. The so-called (0, 0) band gives only $B_{1/2}$ and to get B_0 one must know α, where $B_n = B_0 - \alpha n$. The correct mass factor for the $B_0 m^2$ term is $(\rho^2 - 1)$.

The $-\alpha n m^2$ term gives the energy arising from the mutual effect of vibration and rotation, and according to the new mechanics is always present. Its mass factor is $(\rho^3 - 1)$. The $D_0 m^4$ term should be written $D_n m^4$, but for our purposes D_0 and D_n can be considered as identical. D is always negative, and this term results from the swelling of the molecule with rotation. So far as I am aware, it has not before been considered in isotope work. I have, however, used it in the present work, and find that the correct mass factor is $(\rho^4 - 1)$. The complete rotational isotope shift is then

$$\nu_2{}^m - \nu_1{}^m = (\rho^2 - 1)(B_0'm'^2 - B_0''m''^2) - (\rho^3 - 1)(\alpha'n'm'^2 - \alpha''n''m''^2) + (\rho^4 - 1)(D_0'm'^4 - D_0''m''^4) \quad . \quad (4)$$

Just as in the case of vibration, if the factor $(\rho^2 - 1)$, applying to the chief term, applied also to the others, the expression would be much simplified. It would be, in fact,

$$\nu_2{}^m - \nu_1{}^m = (\rho^2 - 1)\nu_1{}^m \quad . \quad . \quad . \quad (5)$$

where $\nu_1{}^m$ is the distance of a given line from its band origin. Now, equation (3) is not a complete expression for the energy. If it were we should find that the experimental value of $\nu_1{}^m$ was identical with the calculated value

$$\nu_1{}^m = (B_0'm'^2 - \alpha'n'm'^2 + D_0'm'^4) - (B_0''m''^2 - \alpha''n''m''^2 + D_0''m''^4) \quad . \quad (6)$$

In the case of accurately measured lines, at some distance from the origin, the observed and calculated $\nu_1{}^m$ values do *not* agree, due to the neglect of the higher terms Fm^6, Hm^8, etc., of the rotational energy function. I am using the following method to avoid this difficulty.

One calculates a rotational shift from equation (5), using the *observed* $\nu_1{}^m$. Let us call this Result A. This result is now to be corrected as follows. Using the known constants B_0', etc., one *calculates* $\nu_1{}^m$ from equation (6), and then calculates the shift from equation (5), giving Result B. Using the *same* constants, one calculates the shift using the more accurate equation (4), giving Result C. Then (Result C—Result B) gives the correction to be applied to Result A. Since the correction is itself a function of $\nu_1{}^m$, the observed and calculated values of $\nu_1{}^m$ must agree fairly well, if the method is to be quite reliable. On the other hand, if the observed and calculated values are identical, equation (4) gives immediately the desired result.

Because of the fact that many of the experimental results are incomplete and as yet unpublished, I shall give them only briefly. The mass 18 isotope of oxygen was first found, by Giauque and Johnston, in the "A" band (0, 0) of atmospheric oxygen. The vibrational shift, as already noted, is only about $-2{\cdot}067$ cm.$^{-1}$. The isotope lines, due to the O^{16}-O^{18} molecule, have been known for some years, and were called by Dieke and Babcock[14] the A′ lines. Giauque and Johnston, in an attempt to explain these lines, in connection with their work on

[14] G. H. Dieke and H. D. Babcock, *Proc. Nat. Acad. Sci.*, **13**, 670, 1927.

the entropy of oxygen, were led to the discovery of the O^{18} isotope. There is one important difference between the O^{16}-O^{16} and the O^{16}-O^{18} molecules. One is symmetrical and the other is not. The first has alternate rotational levels entirely missing, indicating that the oxygen nucleus has no spin momentum, while the second should have all levels present. Hence O^{16}-O^{18} should show twice as many lines, twice as closely spaced, as the familiar O^{16}-O^{16} molecule. Some of these extra lines had been observed by Dieke and Babcock, but had not been published, since they apparently did not fit into the band. In other words, the A′ series of O^{16}-O^{18}, as published, was precisely like the strong A series of O^{16}-O^{16}, aside from the isotope shift, but the true A′ series consists of twice as many lines. These extra A′ lines have now been published by Giauque and Johnston [1(b)] and by Babcock.[3]

A second series of still fainter lines in this (0, 0) band of oxygen was later found by Babcock [3] and shown by Giauque and Johnston [2] to be due to a second isotope molecule O^{16}-O^{17}. From Babcock's measurements of relative intensity, the abundance of O^{16} is about 1250 times that of O^{18} and 10,000 times that of O^{17}. This is based on the assumption that the coefficient of absorption, per molecule, of the non-symmetrical isotope molecules is the same as that of the ordinary symmetrical O^{16}-O^{16} molecules. As pointed out by Giauque and Johnston,[2] the electric moment of a non-symmetrical molecule *may* give a greater absorption coefficient. Hence the figures for the abundance of O^{17} and O^{18}, as just given, are to be taken as upper limits. It follows from this that Aston's measurement of mass, based on O^{16}, as exactly 16, should be *greater* than the chemical atomic weights, based on the oxygen mixture as exactly 16, by *not more than* one part in 10,000. This seems to be true.

In order to obtain a good estimate of the mass of the O^{17} and O^{18} isotopes, one needs a large observed vibrational shift. Babcock has now found a B′ series of lines in the B atmospheric band (1, 0). For this band I get a calculated vibrational shift of $-36{\cdot}75$ cm.$^{-1}$, based on exact 16 and 18 masses. Babcock's measured shift, with the rotational portion subtracted out, averages $-36{\cdot}82$ cm.$^{-1}$. This is a preliminary calculation, based on a preliminary set of measurements, and is subject to slight revision. It is quite necessary, in the case of this band, to use the accurate equation (4), instead of the approximate equation (5), in calculating the rotational shift. The result already given for the (0, 0) band seems to indicate practically zero electronic shift. The discrepancy in the case of the vibrational shift of the (1, 0) band can then be removed by assuming 16·0000 and 18·0042 as the two masses. If the oxygen mixture is to remain as even 16, the two masses become roughly 15·998 and 18·002.

There still remains one source of uncertainty in these oxygen results. The vibrational constants of the normal level of oxygen are unfortunately not known with the desired accuracy. This point is discussed more fully in my other paper, on Heats of Dissociation. It may very well be the case that the constants now being used are slightly in error, and that there is actually in the atmospheric bands of oxygen a small electronic shift. The mass calculation just made is not affected by this uncertainty.

The results obtained by Dr. King and myself for the carbon isotope, mass 13, are briefly as follows. We first found this in the (1, 0) Swan band, at λ4737. The two molecules concerned are C^{12}-C^{12} and C^{13}-C^{12}. The band appears very faintly, 7·52 Å. to the red of the main band, both

bands being degraded to the violet. The spectrogram is a first order, 15 ft. grating exposure, taken with King's high temperature furnace. In the short interval of 7·5 Å. (about 2 mm. on the plate) it is possible to recognise about six lines and to compare their positions with the corresponding lines of the main band. Because of the extreme faintness of the lines, accurate work is very difficult. Since sending our letter [7] to *Nature*, further observations have been made, and I feel now fairly certain that the measured shift is larger than the calculated by possibly some 0·13 cm.$^{-1}$. How much of this discrepancy (if actual) is due to electronic effect, and how much to a mass ratio not exactly 13 to 12 will be the subject of further work. Incidentally, the present interpretation of the faint Swan band furnishes the final proof that this band system is due to C_2, a matter which has been debated for more than half a century.

If the C^{13} isotope exists, it should be found in all band spectra containing carbon. For work like this, absorption or furnace plates seem far superior to arc spectra emission plates. The latter, due to irradiation, generally conceal all very faint lines. Using absorption plates of carbon monoxide, taken by J. J. Hopfield with a vacuum spectrograph, I found [8] the expected isotope in a long series of bands, from (2, 0) to (15, 0). In this case only the vibrational shift is measured, since the fine structure of the bands is unresolved. Fortunately the head of each band is, theoretically, close to the origin, so that the rotational shift for the head is insignificant. It has not been possible to decide whether C^{12}-O^{18} is present, in addition to C^{13}-O^{16}. I *think* both are present, but because of the relative positions of the two isotope bands, it is possible to prove the presence of the first, but not of the second.

I have found the C^{13} isotope also in the λ3883 (0, 0) band of CN, using a furnace spectrogram originally described by King [15] in 1921. In this case the dispersion is very great (third order of a 30 ft. grating, giving 1·729 mm. per Å.) and the lines are sharp. The entire difficulty of measurement is due to the faintness of the lines; indeed, King in his original article stated that they were just too faint for measurement. By using an especially low magnification in the comparator and having other mechanical conditions favourable, I have found it possible to measure six doublets. All others are concealed by lines of the main band. In this case the rotational constants are accurately known, and the rotational energy shift changes according to theory. The vibrational constants are based on experimental work by different investigators, and there is a bare possibility of unsuspected error. If they are correct, all lines show a shift about 0·05 cm.$^{-1}$ in excess of that calculated, pointing to an electronic effect of this magnitude. To check the mass of the carbon 13 isotope, it is necessary to use bands further removed from the origin of the system. Dr. King writes me that he has now found an extremely faint head 1·45 mm. to the red of the head of the λ3590 (1, 0) band. The calculated position is about 1·42 mm. to the red. This isotope head is too faint for any detailed analysis.

In conclusion, it may be stated that the existence of the mass 17 and mass 18 isotopes of oxygen, and of the mass 13 isotope of carbon, has been conclusively established. In the light of such evidence, it seems probable that *all* elements have isotopes, although the agreement of Aston's mass determinations with the usual chemical atomic weights proves that any as yet unknown isotopes must be present in very small amounts. For the detection of such faint isotopes, the band spectrum

[15] A. S. King, *Astrophys. J.*, **53**, 161, 1921.

analysis seems far superior to the mass spectrograph. In the latter, any impurity is likely to lead to false interpretations, but since each molecule has its own spectrum, impurities in spectra are immaterial, except in so far as they obscure the lines desired. It should be noted, however, that band spectrum analysis gives only the *relative* masses of two isotopes. To obtain absolute masses, the mass-spectrograph must be used. To those of us who have worked for many years, trying to measure and explain *all* the lines of band spectra, both faint and strong, the present results are particularly gratifying. They furnish a most beautiful verification of our present ideas regarding molecular structure, quite aside from their usefulness in establishing the existence of isotopes.

University of California.
3rd July, 1929.

THE ISOTOPE EFFECT IN THE ABSORPTION SPECTRUM OF IODINE MONOCHLORIDE.

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1. Introductory.

The vapour of iodine monochloride at room temperature or a little above is of a reddish-brown colour somewhat resembling that of bromine; the absorption spectra of both have the same general characteristics and lie in much the same region. Each comprises several overlapping vibrational progressions extending from the green to the red end of the spectrum; the most refrangible of these, originating with the lowest vibrational state of the molecule, tends to a limit (the "convergence point"), situated at about λ 5735 for ICl and about λ 5107 for Br_2. Beyond this there is in each case a region of continuous absorption. The isotopic character of Cl and Br should give rise to double bands in ICl (due to ICl_{35} and ICl_{37}) and triple bands in Br_2 (due to Br_{79} Br_{81}, Br_{79} Br_{79} and Br_{81} Br_{81}. The latter effect has not yet been observed, although the vibration structure has been analysed by Kuhn.[1] The vibration structure of the ICl spectrum was first analysed by Gibson and Ramsperger,[2] but no isotopic effect was noted. Wilson [3] published some rather more extensive measurements a little later, and observed five heads which were actually due to ICl_{37}, although he failed to recognize them as such on account of an error in his application of the theoretical formulæ. Gibson,[4] however, observed eleven members of the first progression of ICl_{37}, and interpreted them correctly. From the variations in the isotopic separation he deduced a value for the absolute numeration of the upper [5] vibration levels which had previously been quite arbitrary, and thence determined the origin of the system. His method of treat-

[1] *Z. Physik*, **39**, 77, 1926.
[2] *Physical Rev.*, **30**, 598, 1927.
[3] *Ibid.*, **32**, 611, 1928.
[4] *Z. Physik*, **50**, 692, 1928.
[5] The terms upper and lower will be used throughout to denote the electronic states associated with the system.

ment, although adequate for his immediate purpose, involves approximations of a somewhat indefinite character, and fails to bring out certain interesting features of the isotopic effect in this type of band system. It has, therefore, seemed desirable to give the results of a more detailed theoretical treatment and to study their application to the ICl band system.

2. The Isotope Effect in Band Spectra.

There are now known many examples of band spectra which exhibit isotope effects. The first case to be detected was in the well-known "first harmonic" vibrational absorption band of HCl at 1·76 μ, in which all the lines appear under high resolving power as doublets. Kratzer and Loomis, in 1920, independently interpreted these as due to the two molecules HCl_{35} and HCl_{37}. The corresponding effect in electronic emission bands was recognised and investigated by Mulliken (1923) in the BO spectrum, and subsequently in the band systems due to CuH, CuI and SiN. Watson studied the effect in the MgH spectrum, and was able to obtain evidence for the half-integral numeration of vibration states of the molecule.[6] The case of SnCl, in which both constituents are isotopic, was studied by Jevons,[7] but the complexity was too great to permit of more than a partial analysis.

In all the above cases the effect is of the same type, the separations of the corresponding isotopic bands being approximately proportional to their distances from the band origin. This type of effect may be considered to be characteristic of the heteropolar molecule, in which the vibrations are approximately simple harmonic and are not greatly changed in frequency by the electronic excitation. In consequence only small changes of vibrational quantum number occur, and the band system groups itself into sequences ($n' - n'' =$ constant), each comprising several heads and distributed roughly symmetrically about the zero sequence ($n' = n''$), which is usually the most intense and is situated approximately at the origin ($\nu_e =$ electronic frequency concerned) of the system.

The appearance of the band system due to a homopolar molecule is very different. Here the vibrations are markedly inharmonic and the change in frequency relatively large, with the result that large changes in vibrational quantum number occur, and the sequences overlap one another to such an extent that they can only be detected by analysis of the spectrum. The most obvious structural feature is now the "progressions," for each of which one vibrational quantum number has a constant value. For example, in an absorption spectrum there is one progression associated with each vibrational quantum number (n'') of the lower (*i.e.*, normal) electronic state of the molecule. The bands constituting such a progression are due to transitions from a particular n'' state to a variety of vibrational states (n') belonging to a higher electronic level. The progressions are identical, except that with increasing n'' they are shifted further in the low frequency direction. That having the lowest n'' thus extends clear of the remainder towards a limit (the "convergence point") where the interval between the constituent bands would be zero. Although this is not actually reached in practice, it is often possible to determine its position by extrapolation

[6] All the work up to this point is summarised in the Report of the National Research Council on Molecular Spectra in Gases, 1927.

[7] *Roy. Soc. Proc.*, A., **110**, 365, 1926.

with considerable accuracy. The corresponding wave-number gives a measure of the work required to dissociate the molecule; this is not, however, the chemical work of dissociation unless the products of dissociation are normal atoms. If either or both are in an excited state, allowance may be made for the energy of excitation, if known, and the dissociation work deduced.[8] In order to determine any other molecular constants, it is necessary to know the numeration of the vibrational states, and this is commonly a difficulty in this type of band system. It may be surmounted in the case of the initial state (n'') in absorption by studying the behaviour of the bands under varying temperatures, and comparing it with the variation in the distribution of vibrational energy calculated from the Maxwell-Boltzmann formula. It is thus usually possible to determine the true value of n'' with reasonable certainty.[1] It is much more difficult to fix the absolute values of n', since the above method is not applicable, and there is no other available of similar generality. There are two cases, however, in which the problem may be soluble. The first is when the molecule can be excited to fluorescence by monochromatic radiation; analysis of the fluorescent spectrum should then lead to the evaluation of n'. The second is when the molecule possesses isotopic constituents, provided that the bands due to each do not differ too widely in intensity. The necessity for the latter proviso arises from the difficulty of locating relatively weak band heads in a spectrum of considerable complexity, where we have not only superposed progressions but several successive bands overlapping in each progression.

The only case, apart from that of ICl, in which the isotope effect has been utilised to obtain the n' numeration in a spectrum of this type is that of Cl_2,[9] where one band due to the less abundant molecule $Cl_{35}\ Cl_{37}$ has been identified by Elliott, and its n' value determined from its displacement relative to the corresponding band of $Cl_{35}\ Cl_{35}$. The treatment which follows is an extension of that employed by Elliott.

3. The Isotope Effect in the Band Spectra of Homopolar Molecules.

The term "homopolar molecule" is intended to convey that the type of system particularly considered here is one in which relatively high vibrational quantum numbers occur, so that the usual approximate expression for the isotopic separation is no longer valid. It is shown in the Report on Molecular Spectra [6] (p. 262) that if the vibrational energy is capable of representation by the expression $hn\omega_0(1 - nx)$ then the isotopic band separation,

$$\nu_1 - \nu_2 = (1 - \rho)\{\omega_0'n' - \omega_0''n''\} - (1 - \rho^2)\{\omega_0'x'n'^2 - \omega_0''x''n''^2\} \quad (1)$$

where $\rho = \sqrt{\mu_1/\mu_2}$, μ_1 and μ_2 being the reduced masses of the molecules 1 and 2, ω_0 is the fundamental vibration frequency (*i.e.*, for $n = 0$) of the less massive molecule 1 and n is its vibrational quantum number. If n' and n'' are small the second term is negligible in practice, and we have the familiar result that the isotopic separation is approximately proportional to the distance in wave-number of the band from the origin of the system.

In the present case it is necessary to retain this term, and for convenience we may write $\omega_0 x = a/2$. We then have

[8] See Sponer, *Ergebnisse exakt. Naturwiss.* VI., 75.
[9] Elliott, *Roy. Soc. Proc.*, A., **123**, 629, 1929.

$$\nu_1 - \nu_2 = (1-\rho)\{\omega_0'n' - \omega_0''n''\} - \tfrac{1}{2}(1-\rho^2)\{\alpha'n'^2 - \alpha''n''^2\}$$
$$= (1-\rho)\{(\omega_0'n' - \alpha'n'^2) - (\omega_0''n'' - \alpha''n''^2)\} \quad . \quad . \quad . \quad (2)$$

approximately, since $\frac{1}{2}(1+\rho)$ differs very little from unity. Thus, for ICl $(1-\rho) = 0{\cdot}0214$, and the error involved in this approximation is negligible in comparison with errors of measurement. Since the vibrational levels are represented by the expression $n\omega_0 - \frac{1}{2}\alpha n^2$, the interval between levels $(n - \frac{1}{2})$ and $(n + \frac{1}{2})$ is $\omega_0 - \alpha n = \omega_n$ (say). Equation (2) may therefore be written

$$\nu_1 - \nu_2 = (1-\rho)(n'\omega_n' - n''\omega_n'') \quad . \quad . \quad . \quad (3)$$

This form is simpler in appearance and convenient for calculation in certain circumstances, but (2) is more immediately useful, since for a given progression (n'' constant) it contains only one variable, n'. It may be noted that ω_n' can be obtained directly from the data, since the band intervals in a progression are identical with the level intervals; its value is the mean of the intervals on either side of the band in question.

In a given progression $\omega_0''n'' - \alpha''n''^2$ is constant and the separation should therefore, from (2) have a maximum value when $n' = \omega_0'/2\alpha'$. If the occurrence of such a maximum can be observed, the true n' values may be derived as follows :—

Suppose that on some provisional numbering $\bar{n}$ of the upper levels (dropping the ′ temporarily for convenience) the maximum separation occurs for the band numbered $\bar{n}_m$, and let the correction required to convert $\bar{n}$ to the true numeration be $+ n_0$. Then $\bar{\omega}_0 = \bar{\omega}_n - \bar{n}\alpha$, and can therefore be found. It is actually the separation of bands having the provisional numbers $-\frac{1}{2}$ and $+\frac{1}{2}$. Also $\omega_0 = \bar{\omega}_0 + \alpha n_0$, ω_0 and n_0 being as yet undetermined.

Now from above

$$n_m = \omega_0/2\alpha, \textit{ i.e. } \bar{n}_m + n_0 = \frac{\bar{\omega}_0 + \alpha n_0}{2\alpha},$$

whence

$$n_0 = \frac{\bar{\omega}_0}{\alpha} - 2\bar{n}_m \quad . \quad . \quad . \quad . \quad (4)$$

Since $\bar{n}_m$ is supposed known and $\bar{\omega}_0$ and α are readily determined, n_0 may be evaluated.

The chief advantage of this method is that it does not require the n'' values to be known, since in all progressions the maximum separation will occur for the same n' although its actual value will differ. Since it does not involve the actual separations it may be specially useful in cases where a systematic error occurs in setting on the band heads which affects the measured separations, but which does not affect the location of the maximum. It is only applicable if a succession of the pairs of heads are accurately measurable in the neighbourhood of the maximum. Otherwise it is better to derive n' from individual well-determined separations by making use of equation (3), which may for this purpose be written $\Delta_n = (1-\rho)\omega_n'n' - \Delta''$, where Δ_n is the isotopic separation $(\nu_1 - \nu_2)$ and Δ'' is the separation of the lower level. Hence

$$n' = \frac{\Delta_n + \Delta''}{(1-\rho)\omega_n}, = \bar{n} + n_0 \, . \quad . \quad . \quad . \quad (5)$$

This is almost the same expression as Gibson uses to evaluate n', except that he omits Δ'' and gives ρ^2 instead of ρ. The latter is apparently

a misprint, however, as he uses the correct numerical value. This method will usually be preferable to the former so long as the n'' values are reasonably certain, and has been applied by Elliott[9] to one of the Cl_2 absorption bands.

It is of interest to note that according to equation (2) the isotopic separation may change sign twice in one progression. For example, the weaker heads may at first lie on the more refrangible side of the stronger, then cross over to the less refrangible side and, after attaining a maximum separation, cross back again before the convergence is reached, as shown in Fig. 2. This has not been observed in the case of ICl, since the progressions are not sufficiently developed, but in a favourable case it should be capable of being verified. The " crossing over " would occur in the first four ICl progressions at the following n' values :

I, 1 and 34 ; II, 3 and 32 ; III, 5 and 30 ; IV, $7\frac{1}{2}$ and $27\frac{1}{2}$.

The higher progressions cannot be obtained in great intensity in ICl on account of the dissociation which takes place when the temperature exceeds 200° C. or so.

In any case, it seems clear that Gibson's conclusion that the isotopic separation should vanish at the convergence limit cannot be strictly valid, on account of the residual separation of the n'' level concerned, which may be very considerable for the higher progressions. But, since the convergence limit is never reached in practice the point is of no practical importance.

In the following sections the isotope effect in the ICl bands is described and investigated by the above methods.

4. The ICl Absorption Spectrum. Experimental Details.

Since the existing data did not appear to be sufficiently extensive or accurate for the purpose of testing the foregoing theory, fresh observations were undertaken. Chlorine from a commercial cylinder was bubbled through water and concentrated sulphuric acid, dried by phosphoric anhydride and passed over iodine until no further action took place. The flow was then stopped and the product gently heated until all the trichloride appeared to be converted into monochloride. This was distilled slowly in vacuo four times, the last third being rejected in each case, into a transparent silica tube 30 cm. long by 3 cm. in diameter, with plane ends fused on. The last distillation was entirely in quartz. In order to obtain sufficient absorption with this length of vapour column it was necessary to heat the tube to between 30° and 70° C., and in the course of preliminary visual observations of the spectrum some curious effects were noted.

The convergence limit of the first progression of ICl lies at about λ5735 Å., and below this there is continuous absorption, which is only partial, however, at temperatures up to 50° C. or so. It was found that the first I_2 progression (convergence at λ4995 Å.) was frequently present, although the amount of dissociation to be expected at these temperatures is negligibly small, according to the observations of Gibson and Ramsperger. Investigation showed that the appearance of I_2 bands was favoured by non-uniformity of temperature in the tube. With the original method of heating this could not be entirely prevented, and the I_2 bands were usually present to some extent. They became very strong if local heating was applied to a part of the tube where ICl had

collected, even though the temperature never approached 200° C., which is stated by Gibson and Ramsperger to be the temperature at which dissociation becomes spectroscopically detectable. It was particularly striking that they were strongly developed by cooling part of the tube with solid CO_2, the rest being at about 22° C. This clearly indicates that the phenomenon is not ordinary temperature dissociation, but is dependent upon evaporation or condensation. It was found that when the tube was arranged in such a way that distillation from one end to the other took place continuously the I_2 bands were permanently visible. On the other hand, they could be completely eliminated by placing the tube in a tank of water, even with the latter heated to 40° C. But a very small temperature inequality sufficed to bring them in again, as for example, that produced by heating the outside of the tank near to one end of the tube. No attempt was made to pursue these observations further, with a view to finding the explanation of this behaviour, but in all subsequent work the quartz tube was enclosed in a much larger iron tube (50 by 15 cm.) packed with asbestos wool and wound externally with nichrome, and no further trouble with iodine bands was experienced.

Plates were taken on four spectrographs, namely a 21 ft. concave grating,[10] a glass two-prism spectrograph of Littrow type, a Hilger E1 quartz spectrograph and a Hilger constant deviation instrument. The source of light used was a Nernst glower, except in the case of the grating, when a carbon arc had to be substituted in order to reduce the exposure time to a reasonable length. Several kinds of plate were tried, the best results being obtained with Ilford Process Panchromatic and Wellington Spectrum Process, developed with hydroquinone. The dispersion of the grating proved to be too large to permit of reliable measurements of the band heads, although it is hoped that work on the rotation structure which is progress may result in the identification of some of the relatively weak ICl_{37} bands. The dispersion of the constant deviation instrument is rather inadequate for the determination of wave-lengths, but the instrument was useful in the preliminary stages of the work. The new measurements were made in part with the glass spectrograph (dispersion about 8 Å. per mm.) and in part with the quartz (about 40 Å. per mm.). More of the weak heads were measurable on the latter plates, although of course with less accuracy. A dispersion somewhere between these two would probably have been most suitable, but was not available.

The relatively low accuracy of measurement of the ICl_{37} heads arises from two circumstances. First, they fall inside the strong bands and are less than one-third the strength of the latter. Secondly, all these bands have rather low intensity at the head, on account of the fact that the R branch turns close to the origin of the band, as in the analogous cases of I_2 and Cl_2. It is thus usually a matter of some difficulty to make accurate settings on the weak heads, and in some cases one cannot even locate them with any certainty, as they appear to be concealed by fortuitous variations of intensity of the integrated rotation structure. However, it was possible to supplement the observations of previous workers to a useful extent, and to improve upon the accuracy of certain of the existing measurements.

5. New Measurements of ICl Band Heads.

An attempt was first made to improve upon the existing measurements of the strong (ICl_{35}) heads with a view to obtaining reliable con-

[10] The property of Mr. Wilfred Hall, to whom our thanks are due.

stants for use in equation (2). For this purpose, ten successive heads of progression I and seven of progression II were measured on two Littrow plates. The mean values were in satisfactory agreement with Wilson's, and appeared to be of about the same order of accuracy. The means of both sets were therefore adopted. The results are given in Table I.

TABLE I.

WAVE-NUMBERS OF HEADS OF ICl_{35} ABSORPTION BANDS.

n'.	Progression I.		Progression II.		Intervals,	
	Wilson.	P and C.	Wilson.	P. and C.	Mean.	O − C.
2			14794·1	14794·2		
			166·7	166·2	166·45	− 1·15
3	15342·3	15341·7	960·8	960·4		
	160·7	161·3	161·8	160·2	161·0	− 0·05
4	503·0	503·0	15122·6	15120·6		
	154·3	154·2	153·5	155·3	154·35	− 0·1
5	657·3	657·2	276·1	275·9		
	148·8	148·8	148·3	148·4	148·55	+ 0·7
6	806·1	806·0	424·4	424·3		
	141·5	141·8	141·7	141·9	141·75	+ 0·5
7	947·6	947·8	566·1	566·2		
	136·5	135·7	136·2	135·8	136·0	+ 1·3
8	16084·1	16083·5	702·3	702·0		
	128·5	128·2	128·6		128·45	+ 0·4
9	212·6	211·7	830·9			
	121·1	121·3	121·0		121·2	− 0·3
10	333·7	333·0	951·9			
	114·2	113·2	115·0		114·1	− 0·8
11	447·9	446·2	16066·9			
	107·4	107·8	108·1		107·8	− 0·5
12	555·3	554·0	175·0			

using Wilson's provisional n' numeration. The measurements of Gibson and Ramsperger appear to be of a lower order of accuracy and are therefore not included. The following new bands were identified on the plates, but were not measured on account of the absence of standard iron arc lines in this region (above 6700 Å.) :

I, 0 ; II, (− 1), (− 2) ; III, 0, 1, 6 ; IV, 0, 1, 2, 3, 4.

Progression IV has not been recorded previously, and was obtained on infra-red sensitive plates with the ICl at a temperature of 100° C. or a little above.

It is perhaps worth noting that the measurements made on the grating plates proved to be distinctly inferior in accuracy, as judged by the regularity of the differences, although the heads looked fairly definite and the grating had at least six times the resolving power of the Littrow spectrograph. It seems unlikely that the results can be much improved upon until a complete analysis of the rotation structure is available.

Assuming the mean intervals to be capable of representation by the expression $\bar{\omega}_0' - \alpha'\bar{n}'$, the constants ω_0' and α' were calculated by the method of least squares, which gave $\bar{\omega}_0' = 184{\cdot}1$, $\alpha' = 6{\cdot}594$. The O − C values derived from this formula and tabulated in the last column of Table I. show a little systematic variation which may be attributed

to the neglect of a small term in $\bar{n}'^2$, but the observations are not sufficiently accurate to determine this reliably. In any case, we need not anticipate any serious error from this cause so long as the application of the formula is confined to the region from which it was derived.

New measurements of fifteen heads of the weaker (ICl_{37}) system were secured, and are given in Table II., together with the already existing

TABLE II.

WAVE NUMBER SEPARATIONS OF CORRESPONDING BAND HEADS OF ICl_{35} AND ICl_{37}.

$\bar{n}'$.	Wilson.	Gibson.	P. and C.	
	I.	I.	I.	II.
2				17·7
3				20·5
4				22·3
5				26·2
6	34·7		34·7	25·9
7	35·5			29·0
8	35·9			
9*	37·6		37·4	
10	38·0	44	35·8	
11		43	36·7	
12		41	36·2	
13		39	36·6	
14		39	36·3	
15		40	32·5	
16		34	31·2	
17		33		
18		33		
19		28		
20		26		

data. For convenience the separations of corresponding heads are tabulated instead of the actual wave-numbers. Numbers 10 to 16 in progression I were obtained from plates taken on the quartz spectrograph, and the remainder from the Littrow instrument. The isotope effect has not previously been observed in progression II, and it is believed that these values are distinctly more reliable than the majority of the others, except for number 5, which is derived from only one plate. No ICl_{37} heads belonging to progressions III or IV were identified.

6. The Vibrational Quantum Numbers in ICl.

We proceed to apply the methods described to determine the n' values; evidence for a revision of Gibson and Ramsperger's n'' values will also be forthcoming, and for the present therefore both numerations will be regarded as undetermined.

Our first method, based upon the location of the maximum isotope separation, would require observations of somewhat greater accuracy than those recorded here. It will be seen from Fig. 1 that a maximum does clearly exist, but any estimate of its position might well be in error by $\pm$ 1 unit in n'. However, taking the likeliest value as somewhere about 10 or 11, say $10\frac{1}{2}$, equation (4) gives $n_0 = +7$ as the correction

* This ICl_{37} head is superposed on II. 12 of ICl_{35}

to Wilson's n' numeration. This happens to be in exact agreement with Gibson's estimate, but is, nevertheless, subject to an uncertainty of, perhaps, $\pm$ 2 units.

The second method gives much more definite results, and although it involves assumptions as to the absolute n'' numeration, this is by no means such a disadvantage as might at first appear. In equation (2) the term $(1 - \rho)(\omega_0''n'' - \alpha''n''^2)$ representing the isotopic separation Δ'' of the lower levels is constant for one progression and can readily be calculated. Using Wilson's values for ω_0'' (381) and α'' (1·4), it is found to be 8·2 cm.$^{-1}$ for $n'' = 1$. Since $\alpha''n''$ is negligible in comparison with ω_0'' for the small values of n'' in question, Δ'' may be taken as proportional to n''. Now, equation (5), $n_0 = (\Delta + \Delta'')/(1 - \rho)\omega_n' - \bar{n}$ should give a constant value for n_0 provided that the correct value has been assigned to Δ'' and apart from experimental error in ω_n' and Δ. If Δ'' is assigned too large a value n_0 will show a systematic increase with $\bar{n}$, especially for the higher values of the latter, since ω_n' decreases as $\bar{n}$ increases. Conversely, a negative error in Δ'' will lead to systematically decreasing values of n_0. We have, therefore, to find the value of Δ'' which gives a sensibly constant n_0, and this should settle both numera-

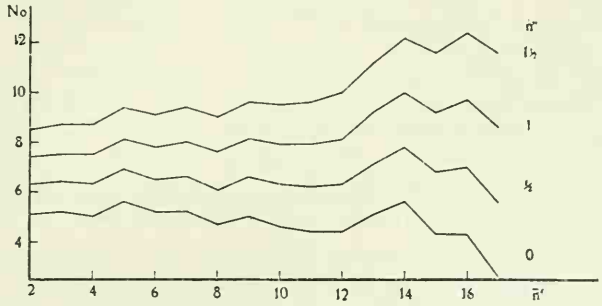


FIG. 1.—Calculated values of n_0, the correction to the provisional numeration n'.

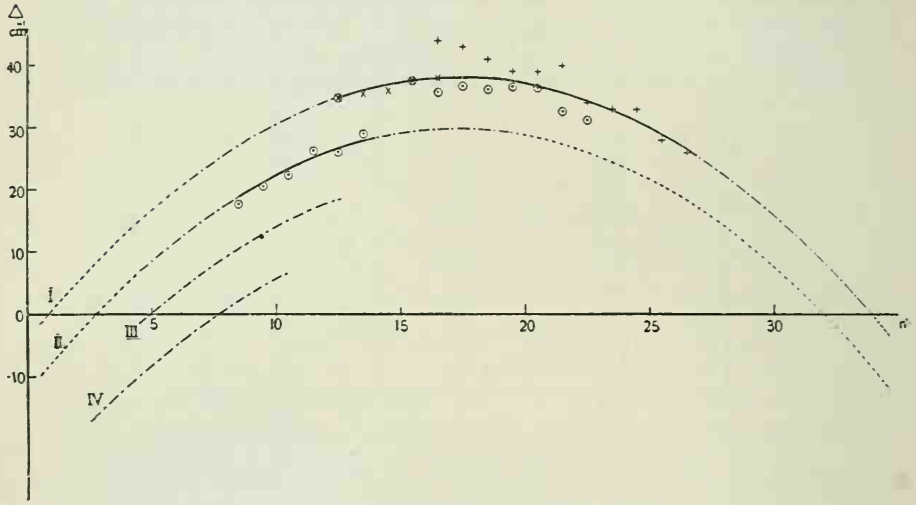
tions at the same time. The only values which could reasonably be assumed for n'' in this case are 0, $\frac{1}{2}$, 1, and 1$\frac{1}{2}$, and Fig. 1 shows the results obtained for n_0, in each of these four cases, using values of ω_n' taken directly from the observed wave-numbers of the ICl_{35} heads, and the new values of Δ, averaged with Wilson's where these are available.

In spite of the rather large experimental uncertainty for the higher $\bar{n}$ values, the result appears quite definite; $n'' = 0$ gives a systematic decrease of n_0, and $n'' = 1$ and 1$\frac{1}{2}$ systematic increases. For $n'' = \frac{1}{2}$ no systematic variation can be detected, and we must therefore conclude that this is the true value. On this basis the mean value of n_0 comes out as 6·55, and we shall therefore take n_0 to be 6$\frac{1}{2}$. The deviations from this value are, of course, rather large for some of the bands under consideration, but it is noteworthy that good agreement exists between the results derived from those isotope heads which appeared to be the most accurately measurable and free from suspicion of blending with other heads, namely Nos. 2, 3, 4 and 6. These give $n_0 = 6{\cdot}3$, 6·4, 6·3 and 6·5 respectively. It is particularly satisfactory that half-integral values are found for both quantum numbers, in agreement with all recent experimental and theoretical results.[11]

[11] See, for example, Watson, *Nature*, **117**, 692, 1926; Jenkins, *Physical Rev.*, **29**, 921, 1927; and Fuess, *Ann. Physik*, **80**, 388.

The isotopic separations to be expected were next calculated on the basis of the new numeration, using equation (1) and the constants already given. They are represented by curves in Fig 2, and the experimental values are also plotted. Apart from Gibson's, which seem to be mostly high, they are well represented by the theoretical expression. Curves are also included showing the calculated isotopic separations for the portions of progressions III and IV, which have been observed. The fact that no ICl_{37} heads belonging to these two progressions were detected is, no doubt, partly attributable to the small values of the isotopic separations, which, in the case of IV, should change sign, *i.e.*, the weak heads cross over to the more refrangible side of the strong ones. Curves were also drawn on the assumptions that $n'' = 0$, 1 and $1\frac{1}{2}$, but, as was to be expected, did not represent the observations so well.

There remains to be considered the discrepancy between our conclusion that $n'' = \frac{1}{2}$ for progression I, and Gibson and Ramsperger's, that



× Wilson. + Gibson. ⊙ P. and C.

FIG. 2.—Relation between isotopic separation Δ and upper vibrational quantum number n'.
——— Signifies that both isotope heads have been observed.
— - — Signifies that only the stronger isotope heads have been observed.
- - - - - Signifies that no isotope heads have been observed.

$n'' = 1$. Their method consisted in photographing this progression at 77° and 200° C. with exposure times so chosen as to give the same photographic density in the two cases, and using, of course, the same concentration of ICl. Calculation on the basis of $n'' = 1$ would require the exposure times to be in the ratio 1·5 : 1, and they found that equal blackening was, in fact, obtained with these relative exposures. The ratio if $n'' = \frac{1}{2}$ would be 1·22 : 1, and so far as one can judge from their account a discrepancy of this order should have been detectable, but the details they give are hardly sufficient to permit of a thorough discussion of possible sources of error. It is desirable that the matter should be further investigated, and it is proposed to repeat their observations using improved experimental conditions. A much longer tube will be employed, in order that the range of temperature may be increased, and microphotometer measurements will be made on as many heads as possible.

7. Constants of the ICl Molecule.

We are now in a position to calculate the fundamental vibration frequency (ω_0', corresponding to $n' = \frac{1}{2}$) in the excited state, and the electronic frequency associated with the band system.

From our value for $\bar{\omega}_0'$, *viz.*, 184·1, and taking $n_0' = 6\frac{1}{2}$, $\alpha' = 6{\cdot}594$, we obtain $\omega_0' = 223{\cdot}7$ as the vibration frequency for $n' = \frac{1}{2}$. Wilson's values for the lower level vibration differences are 381·2 for I-II, and 378·8 for II-III, whence $\alpha'' = 1{\cdot}4$. Assuming that $n'' = \frac{1}{2}$ for I, the associated vibration frequency will be 381·2 + 0·7, or 382 say, $= \omega_0''$. The decrease in the binding force due to excitation is thus very considerable. Taking the force to be proportional to the square of the vibration frequency it decreases in the ratio 2·9 : 1 approximately. The corresponding ratio for Cl_2 deduced from Elliott's recent data is about 3·2 : 1, and for I_2 2·8 : 1.[12] Similar data for Br_2 are not yet available, but the close correspondence of these three results is rather striking. Analysis of the rotation structure may be expected to disclose a considerable increase in the moment of inertia of the ICl molecule as a result of excitation, since Mecke has found that in such cases as this it varies nearly inversely as the vibration frequency. From a preliminary examination of the grating plates it appears probable that each band consists of P and R branches only, the latter running to a head. If the change in the moment of inertia is as large as anticipated, the turning point of the R branch, on which we must presume our settings to have been made, will lie so close to the origin that no sensible error is likely to have been introduced by dealing with band heads throughout instead of the band origins.

The electronic frequency ν_e may be obtained from the wave-number of any band head by equating it to the expression

$$\nu_e + n'\omega_0'(1 - x'n') - n''\omega_0''(1 - x''n'').$$

Using the constants and numeration adopted, we obtain from I 4 and II 5, two particularly well-determined heads, the values 13674·0 and 13673·9 for ν_e. We shall therefore take ν_e as 13674 cm.$^{-1}$, or 1·69 volts (*cf.* Gibson, 1·67 v.). Since the convergence limit is at about 17430 cm.$^{-1}$ (Wilson) the dissociation potential of the excited ICl molecule is 0·46 v.

Summary.

(1) It is shown that in the band spectra of isotopic molecules where relatively large changes of vibrational quantum number occur, the isotope effect should differ markedly from that in band systems involving relatively small vibration changes. The isotopic separation of band heads should reach a maximum for a particular value of n', which is the same for all values of n'', and the true n' values may be derived from the position of this maximum if it can be located with sufficient accuracy. They may also be calculated from individual separations if the n'' numeration is known.

(2) New measurements of a number of ICl_{35} and ICl_{37} heads are given, and used, in conjunction with existing data, to verify the above conclusions and to obtain the true vibrational quantum numbers.

(3) The correction to the provision n' values of Wilson is found to be $+ 6\frac{1}{2}$.

(4) Evidence is presented that the n'' value for the first progression is probably $\frac{1}{2}$ instead of 1 as concluded by Gibson from his investigation

[12] From data tabulated in the Report, p. 231.

of the effect of change of temperature on the absorption. Thus, both vibrational quantum numbers appear to be half-integral, in agreement with recent experimental and theoretical developments.

(5) The values of the fundamental vibration frequencies of ICl are 382 cm.$^{-1}$ for the normal molecule and 224 cm.$^{-1}$ for the excited molecule. The corresponding decrease in the binding force (about 2·9 : 1) is much the same as in the Cl_2 (3·2 : 1) and I_2 (2·8 : 1) molecules. The electronic frequency associated with this band system is 13674 cm.$^{-1}$ (1·69 volts).

THE RECOMBINATION SPECTRA OF HALOGENS AND THE PROBABILITY OF MOLECULAR FORMATION FROM THE ATOMS.

By V. Kondratjew and A. Leipunsky, *Physik.-Techn. Röntgen Institut, Leningrad.*

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The problem of combination of atoms into molecules has only very recently become an object of experimental study. Theoretical considerations, based on data as to the optical dissociation of diatomic molecules, show that the formation of a homeopolar molecule from two atoms can proceed in a single elementary process only in the cases when one of the two combining atoms is excited. One can conceive that the large value for the life-period of active hydrogen and nitrogen arises from this cause. The above-mentioned fact is not, however, the only reason for the low reaction velocity of formation of molecules from atoms. Beutler and Polanyi [1] have shown that in the case of the formation of heteropolar molecules from atoms, where a preliminary excitation is not necessary, the combination of atoms does not take place at every collision (even if it does take place at all in such a way). The authors have shown that the same phenomenon occurs in the case of homeopolar molecules (halogens).

The study of the thermo-luminescence spectrum of various halogen vapours excited in an exhausted tube of fused quartz heated to 1000° C. has shown that this spectrum corresponds completely with the absorption spectrum of corresponding halogen. The long-wave part of the spectrum consists of the bands which are followed by a continuum in the short-wave part. The band spectrum may be considered to result from simple thermal collisions between molecules (this type of excitation is responsible for the band spectrum of sulphur which was obtained by Rosen [2] in conditions similar to ours). The continuum is thought by the authors to arise from the recombination of atoms which proceeds according to the scheme :

$$X + X' \rightarrow X_2 + h\nu$$

in which X is an atom of halogen, and X' an excited atom. This process is a complete reversal of the process of photo-dissociation which was discovered by Franck and his co-workers.

The authors have determined the probability of such a process in the case of bromine. This was done in the following way. When the

[1] *Z. Physik*, 47, 379, 1928. [2] *Ibid.*, 43, 69, 1927.

temperature and pressure of the bromine vapours are known, the degree of dissociation may be calculated and, therefrom, the number of collisions between the normal and excited atoms can be obtained easily. Let this number of collisions be :

$$N_o = Zn^2 e^{-\frac{A}{RT}},$$

where Z is the number of collisions per atom, n the number of bromine atoms per c.c. and A the energy of excitation for atomic bromine, which is 10,400 cal. ($^2P_{\frac{1}{2}} - {}^2P_{\frac{3}{2}}$). The intensity of the black body radiation was determined at such a temperature that it produced the same blackening on a photographic plate in a spectrograph as the thermoluminescence itself (both in the region of continuous spectrum, *i.e.*, from λ 5107 Å. to λ 4300 Å.). Now, taking into account the absorption of light in bromine, one could estimate the number of quanta emitted during one second as a consequence of the reaction :

$$\mathrm{Br} + \mathrm{Br}' \rightarrow \mathrm{Br}_2 + h\nu.$$

Let this number be N. Then the probability γ of the formation of a molecule Br_2 in a single elementary process will be determined by the ratio

$$\gamma = \frac{N}{N_o}.$$

In this way we find for γ the value $0{\cdot}4 \times 10^{-9}$. One can only speak, it is true, of the order of magnitude of γ.

The value of γ may be estimated in another, quite independent, way. It can be shown by means of the principle of detailed balancing that the value of γ is of the same order of magnitude as the value of β in the expression for the velocity of photodissociation :

$$\beta \frac{\rho_\nu}{h\nu} n,$$

where ρ_ν is the density of radiant energy and n the number of molecules per c.c. ; β is connected with the absorption coefficient x in the following way :

$$\beta = \frac{4\pi}{\lambda} \frac{M}{N} cx,$$

where λ is the wave-length, M molecular weight, N is the number of molecules per mol. and c the velocity of light. In the case of bromine we obtain for β the value 10^{-8}. Thus, for γ we get as an order of magnitude :

$$(0{\cdot}4 - 10) \times 10^{-9}.$$

Such a small value of γ shows that the process

$$X + X' \rightarrow X_2 + h\nu$$

is very rare. It renders certain facts concerning atomic reactions comprehensible. For example, it explains why the Br_2 molecules are formed out of the atoms only by means of " Dreierstoss," as was shown by Yost and Jung.[3]

[3] *Z. physikal. Chem. Abt. B*, 3, 83, 1929.

THE ABSORPTION SPECTRUM OF CHLORINE DIOXIDE.

By C. F. Goodeve and C. P. Stein.

Received 10*th September.*

In order to provide a means of identification of chlorine dioxide and to correlate, if possible, its photo-chemical and spectroscopic properties, a study of its absorption spectrum has been made. It was hoped that spectroscopic evidence would be found which would throw light on the mechanism of the formation of the higher oxides of chlorine, known to be formed on illumination of the dioxide. The band system in the absorption spectrum of chlorine dioxide has been found to show considerable regularity, and forms an interesting example of absorption by a triatomic molecule.

The first definite study of the chlorine dioxide bands was made by Miller,[1] who reproduces a sketch of their appearance. Accurate measurements of the positions of the band heads were first made by Käbitz,[2] who measured the positions of forty-nine bands in the visible. About half of these bands he arranged into four series, two strong and two weak series. His arrangement is, however, not in agreement with observations made in the present research, in particular with regard to intensity. General agreement has been obtained in the positions of the band heads measured by Käbitz, with the exception that the existence of a number of his unarranged bands have not been confirmed. The positions of a few have been corrected and better agreement in the series obtained. Käbitz stated that the series spectrum of chlorine dioxide was not in agreement with Deslandres' Law, but Mayer [3] showed that this was due to his misconception of the law. Mayer has given a theoretical interpretation of the series spectrum, based on Käbitz's arrangement.

Experimental.

The preparation of chlorine dioxide was carried out entirely at low temperatures, by the action of sulphuric acid on potassium chlorate. The gas was fractionated a number of times, and dried with phosphorus pentoxide. On account of the photo-chemical decomposition of the oxide, the sample in the absorption tube was replaced after a short period of illumination. Analysis showed the purity to be generally better than 98 per cent.

The absorption cell consisted of a glass tube, 21 cm. long, with ground-on quartz windows, lubricated with a trace of sodium silicate. The pressure of the gas was measured on a manometer filled with metaphosphoric acid. Whenever possible, the photo-decomposition of the gas was reduced by filtering with 4 cm. of chlorine gas at atmospheric pressure.

[1] W. A. Miller, *Phil. Mag.*, **27**, 81 (1845).
[2] B. Käbitz, *Diss. Bonn*, 1905.
[3] H. Mayer, *Z. physik. Chem.*, **113**, 220 (1924).

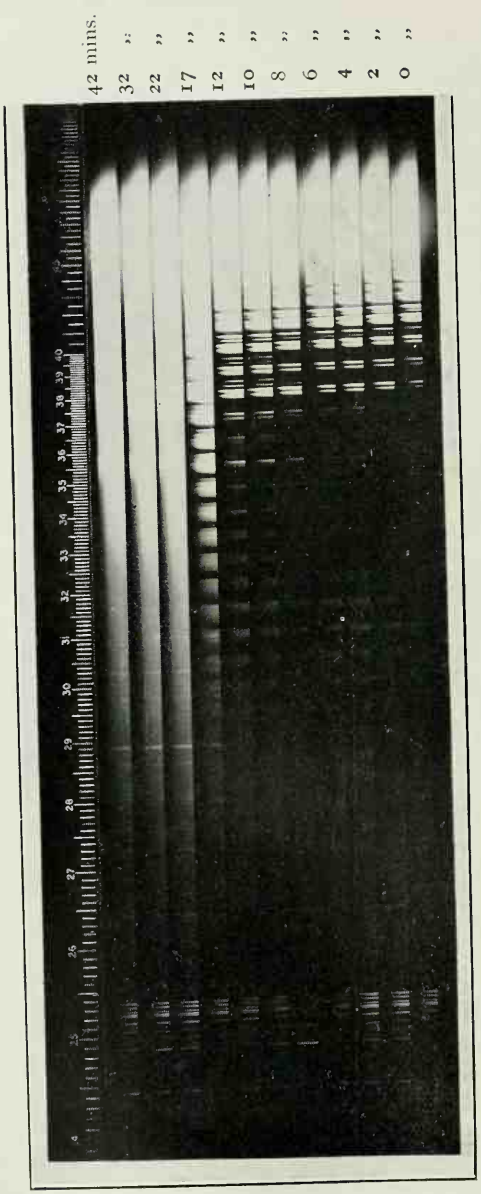

PLATE I.

[*To face page* 739.

In the visible region, a Hilger Constant Deviation Spectrograph was used, with Ilford ordinary and panchromatic plates. A pointolite lamp was used as a source of continuous light, and the iron spark as a comparison scale. Pressures up to 750 mm. of chlorine dioxide were used.

In the near ultra-violet a Hilger E. 3 Quartz Spectrograph was used, with the positive crater of a 10-ampere carbon arc as a continuous source, and a zinc-cadmium-lead spark for comparison. Comparisons were also made with the spectrum of the carbon arc. Pressures from 0·02 mm. to 10 mm. of the gas were used.

In the ultra-violet region from 2200 Å. to 2700 Å., a double prism arrangement was used to prevent fogging of the plates by light scattered in the spectrograph during the long exposure required. The positive crater of a carbon arc was focussed through the absorption cell on the wide-open slit of a Hilger Monochromator. A range of about 150 Å. in any desired part of the spectrum could, with this instrument, be focussed on the slit of the quartz spectrograph.

Preliminary experiments showed band structure extending into the ultra-violet as far as 2650 Å., with a maximum of intensity at about 3400 Å. The bands were degraded towards the red. The spectroscopic detection of chlorine dioxide has been found to be very sensitive, the bands being detectable at pressures below 10^{-2} mm. in 21 cm. of gas layer.

Photographs were taken at varying times of exposure at each successive increase of pressure, covering the entire range described above. The positions of the band heads on each plate were measured with a travelling microscope, a weighted mean was taken for the position of each band, and the wave-length and frequencies were calculated. The heads of the bands are not perfectly sharp, and increasing pressure causes a slight shift in their apparent positions in the direction of increasing frequency. This sometimes amounts to as much as 10 wave-numbers. The mean obtained gives the position of the band head when its intensity was moderate, and in the majority of cases this position could be repeated within a few wave-numbers. In the far ultra-violet, the band head position could only be obtained within about 15 wave-numbers. The last few bands in this region show no heads, the absorption fading out before the head position is reached. The position measured is that of the edge of the band.

The Chlorine Dioxide Series Spectrum.

The band system in the chlorine dioxide spectrum can be seen in Plate I. The first exposure was taken with fresh chlorine dioxide at 10 mm. pressure, and the subsequent exposures after the intervals noted, the gas being under continuous illumination from a 10-amp. carbon arc. As can be seen from the Plate, the photo-decomposition of the gas is very rapid, no trace remaining after twenty-two minutes' exposure.

The absorption spectrum of chlorine dioxide has been found to consist of sequences of bands occurring at regular intervals. Each sequence is made up of four principal bands, whose intensity decreases generally with increase in frequency. All bands are degraded towards the red. These bands form series, primary, secondary, etc., continuing throughout the spectrum, and the members of these series have a common frequency difference, a "sequence difference," between them of about 665 waves per cm. The primary band of each sequence is here determined experimentally, being the first band of the group to appear as the

pressure is increased, and has not necessarily a theoretical foundation. On this definition, Käbitz's first sub-series becomes part of the primary series, and his first and second principal series become parts of the quaternary and tertiary series respectively of the new system.

A typical sequence in the near ultra-violet range is shown diagrammatically in Fig. 1, in which the approximate intensity of absorption is plotted against the frequency, taking the position of a primary band head as zero. The intensity of a band increases to its head, where it drops sharply away. The tail of each band evidently overlaps the preceding bands. At very low pressures only the peaks of the primary bands in the central region are visible. On increasing the pressure, the primary bands become more intense, and increase in number in both directions, while secondary bands make their appearance. Finally, all four series are present. At higher pressures the tails of the secondary bands give complete absorption, and therefore obliterate the primary bands, and at very high pressures the central part of the band system is completely absorbed.

The band sequences in the visible are very similar to those in the ultra-violet, but one important difference becomes apparent. The intensity of the tertiary member becomes very nearly equal to that of the primary member, and the intensity of the secondary member becomes

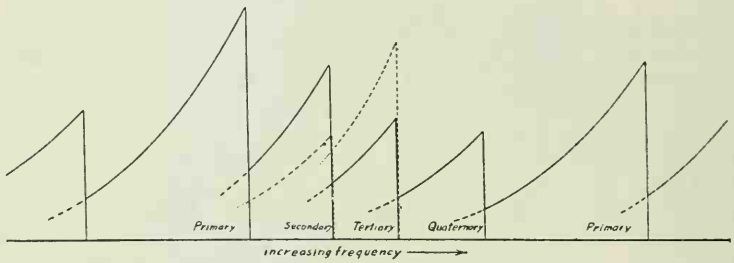

FIG. 1.—A Diagrammatic Representation of a Typical Sequence in the Ultra-Violet.

comparatively low. The former change occurs over a few sequences at about 3900 Å., while the latter is a more gradual one, occurring in the visible. There is no marked change in the relative intensity of the quaternary bands. These changes can be seen in Plate I., and are represented by the dotted lines in Fig. 1.

The wave-numbers corresponding to the positions of the heads of the members of the principal series in the spectrum of chlorine dioxide, as measured in this investigation, are shown in Table I. It will be observed from the table that this spectrum is unusually regular. There is a common series difference (horizontal difference) between neighbouring members of any two series, and a common sequence difference (vertical difference) between neighbouring members of any two sequences. In both cases, however, there is a slight decrease in the value of the differences with an increase in frequency, indicating a convergence of the series. In the case of the primary series, this convergence is very marked. Thirty-two members of the primary series and thirteen, seventeen, and fifteen members of the secondary, tertiary, and quaternary series respectively, have been measured. The absence of members of the latter series in the far ultra-violet does not indicate their non-existence, but probably that the experimental conditions for their appearance was not realised, and perhaps cannot be realised.

TABLE I.—The Principal Band Series of the Chlorine Dioxide Absorption Spectrum.

Sequence.	Primary Series.	Diff.	Secondary Series.	Diff.	Tertiary Series.	Diff.	Quaternary Series.
0							19,423
							656
1	19,635						20,079 (+51)
	706						707
2	20,341 (+27)						20,786 (+49)
	682						697
3	21,023 (+47)				21,310	173	21,483
	710				706		695
4	21,733 (+36) ← Sub-series Ia →				22,016	162	22,178
	704				695		691½
5	22,437 (+20)	143	22,580	131	← Sub-series IIb → 22,711 (−8)	158	22,869 (−13)
	687		697		691		687½
6	23,124 (−8)	153	23,277	125	23,402 (−11)	154	23,556½
	688		690		682		676
7	23,812 (−16)	155	23,967 (−23)	117	24,084 (−22)	148	24,232
	683		674		679		672
8	24,495 (−24)	146	24,641	122	24,763 (−25)	141	24,904
	675		672		673		671
9	25,170 (−29)	143	25,313 (−29)	123	25,436 (−39)	139	25,575 (−31)
	673		666		671		667
10	25,843 (−33)	136	25,979 (−31)	128	26,107 (−42)	135	26,242 (−34)
	660		669		657		658
11	26,503	145	26,648	116	26,764	136	26,900 (−40)
	660		654		660		650
12	27,163	139	27,302	122	27,424 (−47)	126	27,550 (−43)
	658		654		655		644
13	27,821 (−49)	135	27,956	123	28,079 (−58)	115	28,194 (−43)
	654		647		645		646
14	28,475 (−51)	128	27,603	121	28,724	116	28,840
	639		633		641		
15	29,114	122	29,236	129	29,365 (−61)		
	631		622		631		
16	29,745 (−59)	113	29,858	138	29,996 (−60)		
	632		619		615		
17	30,377 (−70)	100	30,477 (−77)	138	30,613		
	637				605		
18	31,014 (−68)				31,218		
	605				629		
19	31,619 (−80)				31,847		
	583						
20	32,202						
	577						
21	32,779						
	557						
22	33,336						
	541						
23	33,877 (−116)						
	464						
24	34,341 (−103)						
	514						
25	34,855 (−109)						
	515						
26	35,370						
	470						
27	35,840						
	420						
28	36,260						
	440						
29	36,700						
	406						
30	37,106						
	403						
31	37,509						
	413						
32	37,922						

Sub-series IIa → (Secondary Series)

Sub-series IIc → (Secondary Series)

Sub-series IVa → (Quaternary Series)

The maximum of absorption occurs at about the fifteenth sequence, which is approximately the centre of the known members of the primary series. The intensities of the sequences decrease slowly on either side of the maximum, while their members follow the relation shown in Fig. 1. The decrease in intensity of successive sequences becomes very much greater in the lower frequency range.

A large number of bands have double heads, the intensity of the second head being about one-quarter of that of the main head, and lying generally to the low frequency side. The positions of these sub-heads were obtained by measuring their separation from the main heads (the average of measurements on a number of plates being used), and these separations are given by the numbers in the brackets in Table I. It is to be expected that sub-heads exist for all bands, but less than two-thirds have been found, the remainder having been obscured by fine structure, or having merged into the general absorption. It will be observed from the table that the separation of the sub-head increases with increase of frequency.

In addition to the members of the principal series, a number of other heads of weak bands make their appearance in different parts of the spectrum. These do not appear to be sub-heads, nor can they be placed in any of the series, either because they appear in parts where sub-heads are already found, or they do not conform to the other sub-heads in regard to relative intensity and separation from the principal head. They have, therefore, been arranged into sub-series, but the possibility of their being merely sub-heads is by no means ruled out. These sub-series are given in Table II., and their positions in the spectrum are indicated in Table I. It will be observed that these series have a series difference (horizontal difference) between their members and the corresponding members of the primary series, and that between the individual members of the sub-series, the sequence difference is the same as that shown by the corresponding members of the primary series. These differences are given in the fifth and fourth columns respectively in Table II. The meaning of the data in the last column will be discussed below.

All bands observed by Käbitz, and by the authors, have been accounted for in the above system, with the exception of a number of the former's unclassified bands. None of these exceptional bands have been confirmed, and may be due to cyanogen emission bands, or to fine structure of the principal bands.

Dèslandres' Law.

The first step in the interpretation of a series spectrum is to obtain an equation by which the series can be expressed. Mayer has given the formula

$$\nu = \nu_0 + 705n - 2{\cdot}9n^2,$$

in which ν_0 has a value corresponding to the first member of the series, and n is the usual series of whole numbers. The series correspond to Deslandres' Second Progressions. The discovery of more bands requires, however, a re-evaluation of the constants.

The values of $\Delta\nu$ shown by members of the primary series have been plotted against the number of the sequence in Fig. 2. These sequence numbers will be identified below with the vibrational quantum levels of

TABLE II.—The Sub-series of the Chlorine Dioxide Spectrum.

1.	2.	3.	4.	5.	6.
Sub-series.	Sequence.	Frequency.	Sequence Difference.	Series Difference.	$-\beta'$.
I*a*.	4	21,849		116	− 588
			693		
	5	22,542		105	− 582
			683		
	6	23,225		101	− 587
			679		
	7	23,904		92	− 591
	Average				− 587
II*a*.	0	19,140		—	− 495
			708		
	1	19,848		213	− 493
			700		
	2	20,548		207	− 475
	Average				−487
II*b*.	1	19,900		265	− 441
			674		
	2	20,574		233	− 449
			709		
	3	21,283		263	− 450
			697		
	4	21,980		247	− 457
			695		
	5	22,675		238	− 449
	Average				− 449
II*c*.	16	29,900		165	− 477
			629		
	17	30,529		152	− 485
			613		
	18	31,142		130	− 477
			607		
	19	31,749		130	− 453
	Average				− 473
IV*a*.	8	24,986		491	− 450
			670		
	9	25,656		486	− 451
			650		
	10	26,306		463	− 458
			665		
	11	26,971		468	− 453
			652		
	12	27,623		460	− 456
	Average				− 454

the activated molecule, and will be designated here by p''.[4] The curve represents the first differential of the equation relating ν to p'', and appears to be made up of two straight lines, meeting at the value for the seventeenth vibrational level. The frequencies of the band heads of the primary series appear, therefore, not to be represented by a continuous function of p'', but rather by two quadratic equations in separate parts of the spectrum. This break in the curve at the seventeenth sequence is important, and will be referred to again.

The constants of these quadratics have been obtained from a large scale plotting of Fig. 2, and have been carefully checked against the observations, agreement well within the experimental error being obtained. These equations are:

$$\nu = 18891 + 722{\cdot}0p'' - 2{\cdot}71p''^2 \ (p'' = 1, 2, 3, \ldots 17) \quad . \quad (1)$$

and

$$\nu = 17340 + 911{\cdot}8p'' - 8{\cdot}42p''^2 \ (p'' = 17, 18, 19, \ldots 32) \quad . \quad (1a)$$

If it can be assumed that the bands follow the second equation beyond the thirty-second member, a value for the convergence limit of the primary series can be obtained. The first differential of the curve becomes zero for a value of $p'' = 54$, giving a frequency value of $\nu = 42{,}023$, which corresponds to a wave-length of 2328 Å. At this point one would expect to find strong continuous absorption commencing, which would indicate that the molecule was dissociated by the absorption of light.

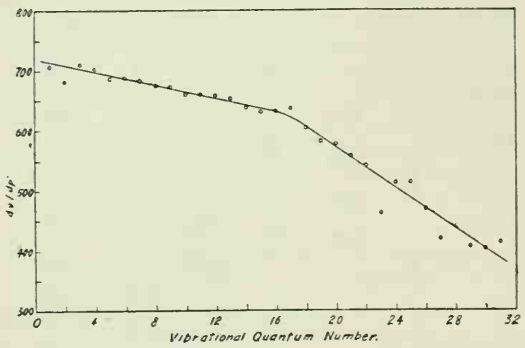

FIG. 2. The First Differential of the Frequency—Quantum Number Equation.

Attempts have been made to investigate the region between the last visible band (2637 Å.) and this convergence limit, by means of the double prism arrangement described above. It was found that continuous absorption commences at about 2800 Å., and increases in intensity towards the ultra-violet. At 2637 Å., with a pressure of 20 mm., 90 per cent. of the light was absorbed continuously. The continuation of the band series probably merges into this continuous absorption. Reproducible results were not, however, obtained, and it would appear that part of this continuous absorption is due to higher oxides of chlorine [5] produced by illumination of the dioxide. No transmitted light at the above pressure in the 2200 Å. region could be detected photographically over long exposures and with very wide slits.

In a similar manner the first differentials of the equations for the remaining three series were plotted against the vibrational quantum numbers, and the constants of these equations calculated. With the ex-

[4] Following the nomenclature used by Griffith and McKeown, "Photo-processes in Gaseous and Liquid Systems" (Longmans). The symbols β'', p'', etc., refer to the upper electronic energy level.

[5] See Bodenstein, Harteck and Padelt, *Z. anorg. Chem.*, 147, 233 (1925).

ception of part of the tertiary series, the frequencies of the band-heads can be expressed by a single quadratic for each series. These equations, including that of the primary for comparison, are as follows :—

Type	$\nu=\nu_0-\beta'+\beta''p''-\gamma''p''^2$.	
Primary	$\nu=18{,}891+722{\cdot}0p''-2{\cdot}71p''^2$ ($p''=1, 2, 3, \ldots 17$) .	(1)
Secondary	$\nu=18{,}891-524+722{\cdot}0p''-2{\cdot}71p''^2$ ($p''=6, 7, 8, \ldots 18$) .	(2)
Tertiary	$\nu=19{,}179+719{\cdot}7p''-2{\cdot}71p''^2$ ($p''=3, 4, 5, \ldots 19$) .	(3)
Quaternary	$\nu=19{,}179-528+719{\cdot}7p''-2{\cdot}71p''^2$ ($p''=1, 2, 3, \ldots 15$) .	(4)

Agreement between the calculated and observed values of ν was again obtained, except that in the secondary series slight deviations occur. The last few members of the tertiary series diverge from the calculated values at about the seventeenth member indicating that a break in the curve exists, similar to that with the primary series. Sufficient members of the tertiary series have not been found, however, to allow a second equation to be built up. The equations have been put in the above form so as to show several striking relationships, the meaning of which will be discussed below.

Theoretical Discussion.

A theoretical interpretation of the absorption spectrum of chlorine dioxide must necessarily, at this stage, be considered as purely tentative, but some suggestions may be made in this connection. It would appear that all the bands of chlorine dioxide belong to one group, and thus correspond to the electronic excitation of a normal unexcited molecule to a single higher quantum level. From the fact that the bands are degraded towards the red, it is concluded that the size of the molecule increases on being raised to the higher electronic state. Quantized changes in vibrational energy accompanying the electronic transition give rise to the individual bands, and their structure is due to quantized changes in rotational energy accompanying the vibrational electronic change. From their number, and the fact that they converge with increasing frequency, the members of the four principal series would at first appear to be derived from four respective initial states of the unactivated molecule, to successively quantized states of the activated molecule. These upper vibration levels have an energy difference of 0·086 volt, or approximately 2000 calories per gram-molecule.

The nature of these initial states is not so clear. It will be observed from Table I. that the series are not equally spaced in the sequences, but if they are arranged in the order—tertiary, primary, quaternary and secondary series, an approximately constant difference of about 950 wave-numbers is obtained. It is, however, improbable that these series, however arranged, can arise from successive vibration levels in the unexcited molecule, because, if the first vibration level is 950 wave-numbers above the zero level, over 90 per cent. of the molecules at room temperature will be in this zero level, and the fraction in higher levels than the first will be vanishingly small. On the other hand, the intensities of the four series are all of about the same order of magnitude.

It is apparent from Table I. that there is a striking relationship between the primary and secondary, and between the tertiary and quaternary series. This relationship is indicated more clearly in the above Deslandres' equations. From the fact that the intensities of the primary and tertiary members of a sequence are equal in the visible,

and nearly so in the ultra-violet, it may be concluded that they are both derived from the vibrationless molecule, but are separated by some secondary effect. There are several possible causes of this separation, but as the molecule of chlorine dioxide has an odd number of electrons, it seems probable that this is an electronic doublet effect. The separation is 288 wave-numbers. This separation decreases slightly as the vibration quantum number is increased, as is indicated by the difference between the coefficients of p'' in equations (1) and (3). This would indicate that the doublet effect is influenced by the amount of vibrational energy contained in the molecule.

Assuming an electronic doublet effect, the assignment of the origins of the secondary and quaternary series to unexcited molecules, containing one quantum of vibrational energy, readily follows. On lowering these series by one place in Table I., a constant horizontal difference of — 524 and — 528 respectively is obtained. These differences are shown in

TABLE III.—Proposed Assignment of Vibrational Quantum Numbers and Doublet Structure to the Chlorine Dioxide Band Spectrum.

Series →	Primary.	$-\beta'$.	Secondary.	Doublet Separation.	Tertiary.	$-\beta'$.	Quaternary.
p''.	$p' = 1$.		$p' = 1\frac{1}{2}$.		$p' = 2$.		$p' = 1\frac{1}{2}$.
$1\frac{1}{2}$	19,635						19,423
	706						656
$2\frac{1}{2}$	20,341						20,079
	682						707
$3\frac{1}{2}$	21,023			287	21,310	— 524	20,786
	710				706		697
$4\frac{1}{2}$	21,733			283	22,016	— 533	21,483
	704				695		695
$5\frac{1}{2}$	22,437			274	22,711	— 533	22,178
	687				691		691
$6\frac{1}{2}$	23,124	— 544	22,580	278	23,402	— 533	22,869
	688		697		682		687
$7\frac{1}{2}$	23,812	— 535	23,277	272	24,084	— 528	23,556
	683		690		679		676
$8\frac{1}{2}$	24,495	— 528	23,967	268	24,763	— 531	24,232
	675		674		673		672
$9\frac{1}{2}$	25,170	— 529	24,641	266	25,436	— 532	24,904
	673		672		671		671
$10\frac{1}{2}$	25,843	— 530	25,313	264	26,107	— 532	25,575
	660		666		657		669
$11\frac{1}{2}$	26,503	— 524	25,979	261	26,764	— 522	26,242
	660		669		660		658
$12\frac{1}{2}$	27,163	— 515	26,648	261	27,424	— 524	26,900
	658		654		655		650
$13\frac{1}{2}$	27,821	— 519	27,302	243	28,079	— 529	27,550
	654		654		645		644
$14\frac{1}{2}$	28,475	— 519	27,956	259	28,724	— 530	28,194
	639		647		641		646
$15\frac{1}{2}$	29,114	— 511	28,603	251	29,365	— 525	28,840
	631		633		631		
$16\frac{1}{2}$	29,745	— 509	29,236	254	29,998		
	632		622		615		
$17\frac{1}{2}$	30,377	— 519	29,858	236	30,613		
	637		619		605		
$18\frac{1}{2}$	31,014	— 537	30,477	204	31,218		
	605				629		
$19\frac{1}{2}$	31,619			228	31,847		
Average		— 524				— 528	

Table III. These two series differences may be considered equal, and represent an energy difference of 1500 calories. The number of molecules at room temperature having a total of this amount of energy in all of their degrees of freedom is small, while the number having this amount of energy in a vibrational degree is still smaller. In the visible, the intensity of any secondary or tertiary band is, indeed, very much less than that of the corresponding vibrationless band in Table III., reaching in the case of the lower frequency bands a relation of about 1 : 50. In the ultra-violet, however, this ratio becomes very much less as one approaches the absorption maximum, attaining a value of about 1 : 4. The factors determining intensity are little understood, and evidence from this source can only be of minor assistance. An attempt will be made to determine the influence of temperature on the relative intensities of these series.

Assuming that the first vibrational level of the unexcited molecule is the origin of the secondary and quaternary series, it is at once noted that its frequency difference of 526 wave-numbers is less than that of the excited molecule (720 wave-numbers). This indicates that the vibrating parts of the molecule are more firmly bound together in the excited than in the unexcited molecule. The direction of degradation of the bands points to an increase in the size of the molecule on electronic excitation, and we are faced with a case in which the molecular binding forces increase as the distance between its parts increases. Such a case is not, *a priori*, impossible, but it is unusual. All possible combinations of these series have been tried, but in no other has anything approaching a constant series difference been obtained. The only other possible value of $\Delta\nu'$ is between 1100 and 1200 wave-numbers, a value very much larger than that of $\Delta\nu''$, and the probability of unactivated molecules containing this energy in vibration, would be exceedingly small. For the present, we must conclude that the binding forces of the chlorine dioxide molecule increase as the diameter of the molecule is increased.

The Sub-Series.

The origins of the sub-series given in Table II. are even more obscure. All attempts at relating these sub-series to one another, and to extend them to more members, have failed. Their origin may lie in the activation of other degrees of vibrational freedom in the chlorine dioxide molecule. If the molecule is triangular, some such effect is to be expected. If these other degrees of freedom are energised in the upper electronic level one would expect a constant difference between the members of any sub-series and the *preceding* primary bands. These differences are recorded in column 5 of Table II., and it is seen that they are not constant. It has been found, however, that the difference between any member of the first four sub-series and the *following* primary band and any member of the last sub-series and the *following* tertiary band is a constant for the sub-series. The differences are negative, and are given in the sixth column of Table II. The sub-series, therefore, follow the Deslandres' equations for the secondary and quaternary series given above. The constants are the same, except that the value of $-\beta'$ is that given in the table for each sub-series.

The similarity of the sub-series to the $p' = 1\frac{1}{2}$ series would indicate that they are derived from some vibrational level above the $p' = \frac{1}{2}$ level in the unexcited molecule. It is to be noted that the sub-series energy

levels are not widely different from the $p' = 1\frac{1}{2}$ level. The nature of these sub-levels must await a more definite knowledge of the structure of the chlorine dioxide molecule.

The Assignment of Absolute Quantum Numbers.

The values of p'' in equations (1) to (4) have been chosen for convenience, and are not intended to represent the absolute values of this variable. These same values, with the addition of the half quantum number required by the wave-mechanics have been included in Table III.[6] The assignment of absolute values to p'' is very difficult, if not impossible, on the evidence available. It was hoped that a limit would be found to the bands. The $p'' = 2\frac{1}{2}$ bands first appeared at 100 mm. pressure in a 21 cm. tube, but an eight-fold increase in pressure disclosed the $p'' = 1\frac{1}{2}$ bands. There is no reason to suppose that a further large increase in pressure or tube length would not disclose more bands. The isotope effect, which will be treated in more detail below, is generally of assistance in determining the absolute $p'' = \frac{1}{2}$ band. The isotope separation becomes a minimum at $p'' = 5\frac{1}{2}$ in the primary, and $4\frac{1}{2}$ in the tertiary series, pointing to these bands as the origins of the series, but the series continue below these bands. The arrangement given in Table III. must accordingly be considered as purely tentative.

This arrangement leaves many problems unanswered. An explanation of the cessation of the secondary series at the sixth vibrational level and of the tertiary series at the third, the prominence of sub-series at low frequencies, and the general lack of agreement in position of the series bands of lowest frequency, to mention only a few, has not been attempted. More experimental evidence, and a further knowledge of the structure of the molecule is necessary before this can be done. It is to be remembered, of course, that the head of a band is not its origin, and bands should only be related, strictly speaking, by their origins. The position of this "null line" is, however, rarely found, but the distance between the origin and the head is generally a constant, or some simple function of p'', and for the purpose of the theory the positions of the heads may be used.

The Isotope Effect.

Double heads in band absorption are generally ascribed to the influence of isotopes on the vibration frequencies of the molecules. Mulliken [7] for the isotopic separation in a diatomic molecule, has derived the equation,

$$\Delta\nu_i = (\sqrt{\mu_1/\mu_2} - 1)(\nu_{p''} - \nu_0),$$

in which $\nu_{p''}$ is the frequency of the principal band head, ν_0 the frequency of the origin, and μ_1 and μ_2 the effective masses of the isotopes. These masses are given by $M_1M'/M_1 + M'$ and M_2M'/M_2+M'. To apply this equation to chlorine dioxide we must assume that the oxygen atoms act as one unit of mass 32, and that the vibration is along a line joining the centre of this unit and that of the chlorine atom. Placing the value for

[6] Note that the primary and tertiary series arise from molecules containing $\frac{1}{2}h\nu$ of energy, instead of from vibrationless molecules.

[7] See "Molecular Spectra in Gases," *Bull. Nat. Res. Council*, p. 262.

the isotopes of chlorine in the above equation, the expression for the separation becomes

$$\Delta\nu_i = 0{\cdot}0130(\nu_{p''} - \nu_0) \quad . \quad . \quad . \quad . \quad (5)$$

The band-heads given in Table I. are naturally due to the more abundant (Cl_{35}) molecules, and, as the heavier atom vibrates the more slowly, the separation of the sub-head should be negative, and its intensity should be about one-quarter of that of the main head. In nearly all cases this is found to be true.

The separation of the sub-heads in the primary series has been plotted against the frequency, and a straight line cutting the zero axis at the $p'' = 5\frac{1}{2}$ band was obtained. The sub-head separation increases only two-thirds as rapidly as required by equation (5), being represented empirically by the equation

$$\Delta\nu_i = 0{\cdot}0089\ (\nu_{p''} - \nu_{5\frac{1}{2}}) \quad . \quad . \quad . \quad . \quad (6)$$

The sub-heads of the remaining three series conform to this equation, except that those of the last two series have their origins in the $p'' = 4\frac{1}{2}$ band. The agreement of observation with theory is satisfactory, considering the assumption that the chlorine dioxide molecule can be treated as a diatomic molecule. The fact that the origin of the isotope effect is not the origin of the series is still without explanation, as is also the fact that some of the sub-heads have a positive separation. These latter only occur with the lowest frequency bands, and are included as sub-heads rather than sub-series, because their intensities relative to the main heads are the same as those of the other sub-heads.

Rotational Fine Structure.

Almost all the bands in the visible and near ultra-violet exhibit, under the proper conditions of pressure and photographic exposure, the fine structure due to quantized rotational energy changes. The measurement of this fine structure has not as yet been attempted, and will meet with considerable difficulty on account of the continuous absorbing background, and the insufficient dispersion of the spectrographs. The following points are, however, worthy of note. Fine structure can be detected in the tails of nearly all bands in the visible region, and in particular, in the bands of the primary series. These bands are narrow and regularly spaced, and diverge slightly towards the red end of the band, and they would appear to be due to the quantization of a single degree of rotational freedom. This would indicate either a straight line molecule, or, if the molecule is triangular, that there is only a small probability of the second degree of rotational freedom being affected. The separation of these fine bands in the fourth to eighth members of the primary series has been measured, and found to be about 20 wave-numbers, with evidence of a slight decrease in this value towards the ultra-violet end of the spectrum. Members of the other series show approximately the same value of $\Delta\nu$ for a rotational quantum change.

Fine structure again becomes prominent in the ultra-violet in the twelfth and fourteenth sequences, but is peculiar in that it shows no divergence as it proceeds towards the tails of the bands. The separation of this fine structure is 14·6 and 9·8 wave-numbers for these sequences, respectively, and would indicate that the size of the rotational quantum decreases, and hence the moment of inertia of the molecule increases as

the vibrational quantum number is increased. It appears from a plotting of the fine structure separation against the vibrational quantum number, that the rotational quantum becomes zero at the sixteenth or seventeenth vibrational level. Resolution of the vibration bands beyond the fourteenth sequence has not been attained, and it would appear that here the rotational energy ceases to be quantized. Such a phenomenon has been termed "predissociation" absorption, and interpreted by Henri as a splitting up of the molecule subsequent to absorption, within a time interval comparable with the period of rotation of the molecule, but much greater than the period of vibration. The vibrational energy would, therefore, continue to be quantized, while the rotational would not.

It is of interest to note that the break in the frequency curve shown in Fig. 2 occurs at approximately the same position in the spectrum as does the predissociation. It may be inferred from the break in the curve that the molecule undergoes some transition on absorption of light of energy great enough to provide more than seventeen quanta of vibrational energy. This transition may be in the electronic orbits, or in the arrangement of the atoms in the molecule. Further evidence is necessary before these two phenomena can definitely be related, or before a decision can be made as to which is cause and which effect, but a marked increase in the moment of inertia just prior to this transition is of particular significance. It is of further interest to note that these two phenomena occur at the point of maximum absorption, but here the connection is more obscure.

Conclusion.

The chlorine dioxide molecule appears to be one of the few molecules of more than two atoms which permit even a partial analysis of its spectrum. This may be evidence in favour of the above proposed view, that the molecule acts as a diatomic molecule, the oxygen atoms being close together, and acting as a unit. The fact that the heat of formation of chlorine dioxide from an oxygen molecule and a chlorine atom is very small, may be considered as further support of this structure. The moments of inertia of the molecule, calculated from the fine structure separation, will be of assistance in this problem when a more detailed examination has been accomplished with higher dispersion instruments.

Summary.

The absorption spectrum of chlorine dioxide has been studied and found to be discontinuous in the visible and near ultra-violet with evidence of continuous in the far ultra-violet. The frequencies of the band heads have been determined. The bands have been classified under three types, principal series bands, sub-series bands, and sub-heads. There are four principal series, whose members fit into Deslandres' equations, which converge towards the ultra-violet. Continuous absorption has been found to occur before the point of convergence of the first principal series has been reached. The origins of these series have been discussed, and an assignment of quantum numbers has been proposed. The origins of the sub-series have also been discussed. The sub-heads have been ascribed to the isotope effect of the (Cl_{37}) atoms. The separation of the sub-head from the principal head increases linearly with the vibrational quantum number at a rate of about two-thirds of that calculated for a molecule in which the two oxygen atoms are close together and act as one.

The molecule of chlorine dioxide appears to undergo a transition in some manner on absorption of radiation sufficient to cause vibration in the seventeenth level or above. A marked decrease in the separation of the rotational fine structure, also takes place at this point and evidence of predissociation has been found. The bearing of these results on the structure of the chlorine dioxide molecule has been discussed.

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BAND SPECTRA AND ELECTRONIC STATES OF SOME METAL HYDRIDES.

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At the present time, the problem as to the nature of the electronic state in diatomic molecules is subject to numerous considerations. Hund [1] entered upon this problem with a thorough investigation as to the adiabatic character of transitions between atomic and molecular states. The essential principles, thus ascertained, he applied to a systematic survey of the electronic levels in molecules,[2] similar to that almost completed in the field of atomic spectra. His views were already embodied in the original discussion of band spectra and electronic states started in 1925 by Birge, Mecke, and Mulliken, and in seeking to relate them more closely to the results of spectroscopic analysis the latter, independently of Hund, turned to the problem of the individual quantum assignments of electrons in molecules.[3,4,5] In his latest paper on this subject, Mulliken deals with the electronic states in diatomic hydrides (MH).

During the course of experimental work on the spectra of metal hydrides, we were greatly interested in the views set up by Hund and Mulliken; we shall therefore discuss these in the light of some new results obtained in this laboratory. In this connection we are primarily interested in the spectra of the neutral or ionised metal hydrides belonging to the first, second, and third group of the periodic table (AuH, HgH, AlH). Our main intention is to show that the stability problems of the hydrides can be treated on the basis of some very simple assumptions.

With regard to the quantum assignments used in the present paper, we refer to the papers cited above.

Methods.

According to the new mechanics, the transitions of separate atoms into molecular bonds constitute an adiabatic process, wherein no electronic states are lost or abruptly changed as the nuclei distance r is varied. In cases of very near approach or intersection of the electronic potential gradients, however, difficulties may arise with regard to the interaction of the different gradients. In the following paragraph, some

[1] F. Hund, *Z. Physik*, **40**, 742, 1927.
[2] *Ibid.*, **51**, 759, 1928.
[3] R. S. Mulliken, *Physical Rev.*, **32**, 186, 1928.
[4] *Ibid.*, 761, 1928.
[5] *Ibid.*, **33**, 730, 1929.

important factors governing the transitions between atomic and molecular states are mentioned.

(*a*) The potential gradients in the molecule are partly reproduced, when we check the vibrational and the rotational terms of the nuclei around their equilibrium distance r_0. In a few cases—the spectra of some hydrides here discussed are favourable—the potential gradients of different electronic states in the molecule can be checked, even up to their states of dissociation. In such cases the atomic origin of the molecular states is fully secured. For nuclei distances smaller than r_0 the potential gradients are, however, soon lost in the enormous field of the repulsive forces of the positive and the negative charges in the molecule. The correlation between molecular states and those of *the combined atoms* ($r = 0$) can therefore only be settled by means of theoretical assumptions.

(*b*) The distribution of the electrons in molecules is governed by the Pauli principle, according to which their number is determined as follows :

$$1s\sigma^2 \quad 2s\sigma^2 p\sigma^2\pi^4 \quad 3s\sigma^2 p\sigma^2\pi^4 d\sigma^2\pi^4\delta^4 \ . \ . \ .$$

When a metal hydride is formed, then the H-electron must be promoted from its (supposed) normal state $1s$ into some, as yet, unclosed shell. According to Mulliken, the amount of promotion energy plays an important rôle in the formation of hydrides, so that large promotion energies should be accompanied by a decrease of the molecular stability.

(*c*) An intermediate molecular state of large stability is formed when the adiabatic transition between the states of the separate atoms into those of the combined atoms involves a large energy drop and *vice versa*. Thus Hund (Ref. 2, p. 789) ascribes the considerable stability of LiH to the transitions :

$$\mathrm{Li} + \mathrm{H} \rightarrow \mathrm{LiH} \rightarrow \mathrm{Be}$$

where the ionisation energy of Lithium (5·37 volts) is small compared with that of Beryllium (9·41 volts).

(*d*) Associating molecular levels with those of the combined atoms, we employ the individual l_τ-conservation rule of electrons, according to which molecular $s\sigma$, $p\sigma\pi$, $d\sigma\pi\delta$-electrons are converted into s, p, d-electrons respectively, in the combined atoms.

(*e*) Comparing a succession of hydrides and elements in the periodic table such as :

$$\mathrm{Au, \ AuH, \ Hg, \ HgH, \ Ta, \ . \ . \ .}$$

we shall find that a corresponding state of the combined atoms generally forms the origin to a molecular state in the succeeding hydride. Taken in this sense, the study of the hydrides offers a fascinating illustration of Bohr's method of deducing the periodic system of elements.

The Hydrides of Copper, Silver, and Gold.

The band spectra of CuH, AgH, AuH are found in emission [6] as well as in absorption spectra,[7] and have been classified as ${}^1\Sigma' \rightleftharpoons {}^1\Sigma$ transition. An additional ${}^1\Pi \leftarrow {}^1\Sigma$ transition is found in the absorption spectrum of

[6] R. Frerichs, *Z. Physik*, **20**, 170, 1923 (CuH) ; E. Bengtsson, *ibid.*, **20**, 229, 1923 (CuH) ; E. Bengtsson, *Arkiv. f. Mat. Astron. Fys.*, **18**, 27, 1925 (AuH); E. Bengtsson and E. Svensson, *Compt. rend.*, **180**, 274, 1925 (AgH).

[7] E. Hulthén and R. V. Zumstein, *Physical Rev.*, **28**, 13, 1926.

CuH.[8] In Table I. all the necessary data for these levels are given. The dissociation values D^v are those calculated by Mulliken [5] from a

TABLE I.

	Term.	Cm^{-1}.	ω_0 $\omega_0 x$.	r_0.	D_t Volts.	H—electron.	M—electrons.	Molecular State.	D Volts.
CuH	$^1\Sigma$	0	1903·7 37·4	1·471	3·02	$3d\sigma$	$3d^9 4s^2\ ^2D'$	$3d\sigma^2\pi^4\delta^4 4s\sigma^2$	3·02
	$^1\Sigma'$	23311·15	1655·7 44·6	1·582	1·89	$4s\sigma$	$3d^{10}4p\ ^2P$	$3d\sigma^2\pi^4\delta^4 4s\sigma p\sigma$	2·2
	$^1\Pi$	44,600	—	1·50	—	$4s\sigma$	$3d^{10}5p\ ^2P$	$3d\sigma^2\pi^4\delta^4 4s\sigma 5p\pi$	2·0
AgH	$^1\Sigma$	0	(1690)	1·630	—	$5s\sigma$	$4d^{10}5s^2S$	$4d\sigma^2\pi^4\delta^4 5s\sigma^2$	—
	$^1\Sigma'$	29,898	(1490)	1·665	—	$5s\sigma$	$4d^{10}5p^2P$	$4d\sigma^2\pi^4\delta^4 5s\sigma p\sigma$	—
AuH	$^1\Sigma$	0	2249·4 34·0	1·54	4·59	$5d\sigma$	$5d^9 6s^2\ ^2D'$	$5d\sigma^2\pi^4\delta^4 6s\sigma^2$	4·59
	$^1\Sigma'$	27342·1	1630 79	1·69	1·04	$5d\sigma$	$5d^9 6s^2\ ^2D'$	$5d\sigma^2\pi^4\delta^4 6s\sigma^2$	1·0
	$^1\Sigma''$	38,230	(1548)	1·70	—	$6s\sigma$	$5d^{10}6p\ ^2P$	$5d\sigma^2\pi^4\delta^4 6s\sigma p\sigma$	1·8

linear extrapolation of the vibrational levels. As seen from the table, these D^v values agree reasonably well with the D which serves to fit the molecular levels into the scheme of atomic levels.

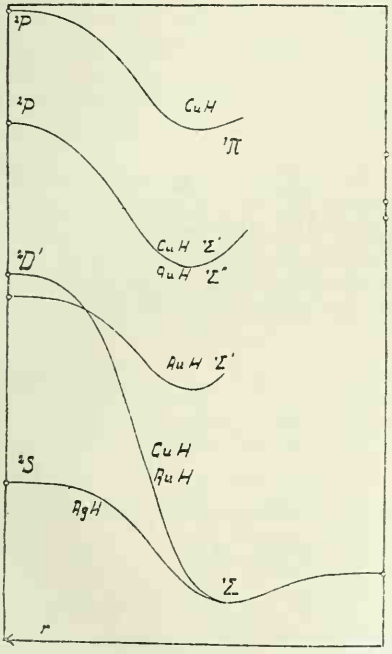

FIG. 1*a*.

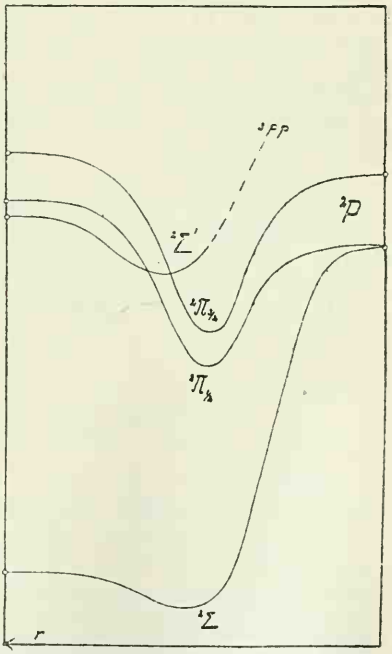

FIG. 1*b*.

Our argument appears better from Fig. 1*a*, where a qualitative drawing of the potential gradients is given, inserted between the

[8] H. Stücklen, *Z. Physik*, 34, 562, 1925. Stücklen reports only two series branches in the band λ 2240. However, on spectrograms taken by Hulthén and Zumstein a third (R)-branch is clearly visible and as interpreted by Hulthén, this band consists of singlet PQR branches having a common $^1\Sigma$ state with the $^1\Sigma' - {}^1\Sigma$ system of CuH.

atomic levels of the separate and the combined atoms. With regard to copper and gold hydride, the proposed quantum assignments deviate from those given by Mulliken, who suggested that the normal $^1\Sigma$-level in all three compounds originates from the normal ^{2}S-state of the separate atoms. But his D-values, thus derived, are less convincing. As a matter of fact, the appearance of the absorption bands does not force us to relate the lower $^1\Sigma$-level to the normal state of the separate atoms. Thus, Duffendack and Black [9] have shown that the $^2D'$-doublet is thermally excited in the vacuum furnace, as indicated by a large number of transitions from these levels into higher excited ones, appearing simultaneously with the CuH bands. A similar test on gold is still lacking, but should prove necessary on account of the higher excitation of its $^2D'$-levels. In any case, the $^2D'$-states in copper and gold, with their incomplete d^9s^2-groups seem to be much more in accordance with a chemical interaction with the hydrogen atom than their normal ^{2}S-states.

The excited $^1\Sigma$-level in CuH should originate from 4^2P in Cu. Again, this arrangement is supported by the observations in the vacuum furnace,[9] transitions from the 4^2P levels appearing *in emission*, simultaneously with the hydride band. These levels are supposed to be excited by absorption of resonance radiation rather than by thermal excitations.[9] In gold hydride the $^1\Sigma'$-level is supposed to originate from the lower component $^2D'$, and the higher excited $^1\Sigma''$-level from 6^2P in Au. Thus, the latter rather than the former should correspond to the excited $^1\Sigma'$-level in CuH. The violet glare observed when the gold nugget is melting in the absorption tube might arise from a $^1\Sigma' \rightarrow {}^1\Sigma$ transition in the hydride.

In silver the d^{10} group is supposed to be much more stable than in copper and gold, and as a matter of fact the $^1\Sigma' \rightleftharpoons {}^1\Sigma$ transition in silver hydride fits well into the $^2P \rightarrow {}^2S$ interval of Ag. It is especially interesting to compare this pronounced dissimilarity of silver *vis-a-vis* gold and copper with results recently obtained in this laboratory on the spectra of Zn^+H [10] and Cd^+H [11] (Table II.). In Zn and Cd the d^{10} groups are

TABLE II.

	Term.	Cm$-^1$.	w_0	w_0x.	D^v.
Zn^+H	$^1\Sigma$	0	1915·8	39·0	2·5
	$^1\Sigma'$	46431·6	1358·4	11·0	($<$ 4·4)
Cd^+H	$^1\Sigma$	0	1776·8	37·8	1·9
	$^1\Sigma'$	42680·0	1248·9	7·3	2·5

supposed to be very firmly completed (Bohr), and consequently a close analogy between the spectra of Zn^+H, Cd^+H and AgH should be expected. The much more reliable data on the vibrational terms in Zn^+H and Cd^+H also indicate [10, 11] that the $^1\Sigma$-levels originate from the ^2S, ^2P-states in Zn^+ and Cd^+.

Applying the l_τ-conservation rule (*d*), we now combine the normal

[9] O. S. Duffendack and J. C. Black, *Physical Rev.*, **29**, 358, 1927 (abstract).
[10] E. Bengtsson and B. Grundström, *Z. Physik*, **57**, 1, 1929.
[11] E. Bengtsson and R. Rydberg, *Z. Physik* **57**, 678, 1929.

$^1\Sigma$-levels of the hydrides here discussed with the normal ^1S-levels in the united atoms (Zn, Cd, Hg, Ga^+, In^+). The large stability of the normal states in CuH and AuH we mainly interpret as due to the large energy drop (c) between $^2D'$ of Cu, Au and ^1S of Zn, Hg. The comparatively small stability of AgH—as indicated by its $r_0\omega_0$-values—is readily explained by the small energy drop between ^2S of Ag and ^1S of Cd. Similar reasons cannot be urged to explain the large stability of the Zn^+H and Cd^+H molecules, but here it seems more reasonable to assume binding forces of purely polar character. In all cases completed d^{10} and s^2 shells are formed within the meaning of London's valence theory.

Hydrides of Bivalent Metals.

The electronic levels known in the band spectra of ZnH, CdH and HgH all originate from the normal ^1S- and the excited ^3P-states in the metal atoms,[12] as shown in Fig. 1*b*. The most likely co-ordination of the excited $^2\Sigma'$, $^2\Pi_{1/2}$, $^2\Pi_{3/2}$ levels into $^3P_0$, $^3P_1$, $^3P_2$ respectively, in the atomic triplet offers a problem not yet discussed from the theoretical point of view. Adopting the quantum assignments given by Hund and Mulliken (Table III.), and applying the l_τ-conservation rule, we combine

TABLE III.

	Term.	Cm.$^{-1}$.	r_0.	D.	H — electron.	M — electrons.	Molecular State.	Combined Atoms.
ZnH	$^2\Sigma$	0	1·608	0·91	$4p\sigma$	$4s^2\,{}^1S$	$4s\sigma^2p\sigma$	$4s^2p$
	$^2\Pi$	23263·6 / 23594·0	1·538 / 1·505	2·03	$4s\sigma$	$4sp\ {}^3P_{12}$	$4s\sigma^2p\pi$	
	$^2\Sigma'$	(29,240)	(2·23)	1·3	$4p\sigma$	$4sp\ {}^3P_0$	$4s\sigma p\sigma^2$?	$4spp$
CdH	$^2\Sigma$	0	1·785	0·67	$5p\sigma$	$5s^2\,{}^1S$	$5s\sigma^2p\sigma$	$5s^2p$
	$^2\Pi$	22271·5 / 23272·1	1·687 / 1·678	1·70	$5s\sigma$	$5sp\ {}^3P_{12}$	$5s\sigma^2p\pi$	
	$^2\Sigma'$	28359·1	2·413	0·91	$5p\sigma$	$5sp\ {}^3P_0$	$5s\sigma p\sigma^2$?	$5spp$
HgH	$^2\Sigma$	0	1·76	0·369	$6p\sigma$	$6s^2\,{}^1S$	$6s\sigma^2\,p\sigma$	$6s^2p$
	$^2\Pi$	24932·8 / 28616·8	1·597 / 1·588	2·16 / 2·28	$6s\sigma$	$6sp\ {}^3P_{12}$	$6s\sigma^2\,p\Pi$	
	$^2\Sigma'$	33876·1	2·02	0·84	$6p\sigma$	$6sp\ {}^3P_0$	$6s\sigma p\sigma^2$?	$6spp$

the $^2\Sigma$, $^2\Pi_{1/2}$, $^2\Pi_{3/2}$ levels with the normal ^2P-doublet of the combined atoms (Ga, In, Ta). On the other hand, a $^2\Sigma$-state showing a tendency to decrease in conjunction with an excited $^2\Pi$-state, both emanating from a common ^2P-state of the combined atoms, illustrates a case theoretically deduced by Hund (Ref. 2, p. 766). The excited $^2\Sigma'$ should be combined with either ^2P or with some excited pp'-level. Their unusually large

[12] E. Hulthén, *Arkiv. f. Mat. Astron. och Fys.*, **21** B. 5, 1929. The dissociation energies here given were calculated from the minimum ($n = 0$) of the potential gradient instead of from $n = \frac{1}{2}$ as here given. Also the D-values given for CaH and MgH were later found to be somewhat too small. W. W. Watson (*Physical Rev.*, 34, 372, 1929) estimates the dissociation energies of CaH, MgH, BeH as respectively 1·9, 2·12 and 3·3 volts. However, the observed data on the first vibrational interval in the normal state of CaH ($\Delta\nu = 1262{\cdot}5$ cm.$^{-1}$) makes this value at least very improbable. Further, we are indebted to Messrs. G. Stenwinkel and E. Svensson for using their unpublished and still somewhat unsettled data on the excited $^2\Sigma'$-states of ZnH and CdH.

r_0-values should also be connected with the latter proposal. According to Mulliken, the extremely small dissociation energy of HgH in its normal state (0·369 volts) is due to the promotion of the hydrogen electron into a $6p\sigma$ state in the molecule. We interpret it directly from Fig. 1*b* as mainly caused by the large increase of term energy between the normal states of Hg and Ta.

As far as can be judged from empirical data,[12] there is, except in the case of CaH, a steady increase of the dissociation energy for the normal states, as we go from HgH towards BeH. This increase is in correlation with the levelling of the term energies between the separate and the combined atoms. Further, some additional excited levels found in CaH should be attributed to extraordinary term relations in the united atoms (Sc).

A Comparison between the Hydrides of Magnesium and Aluminium.

The band spectra of Ga, In, and Ta-hydrides are not known, so we are not able to continue our comparison between the electronic level

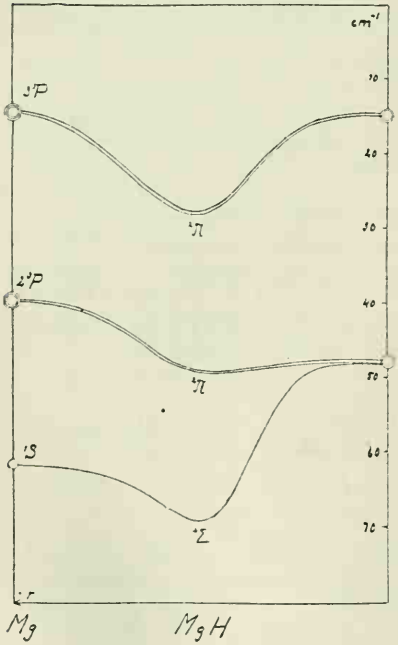

FIG. 2*a*.

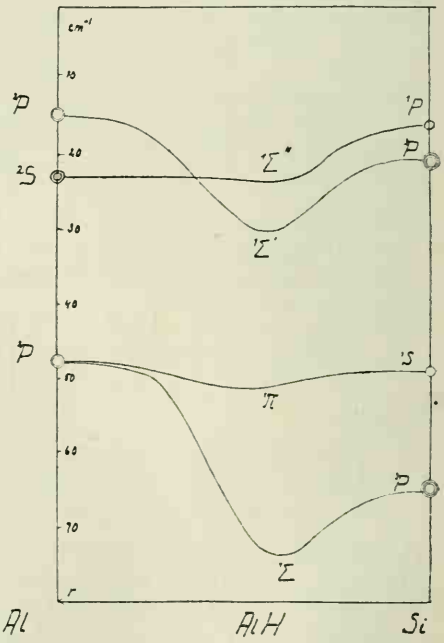

FIG. 2*b*.

of alternating atoms and hydrides started at Cu, Ag, Au. The band spectra of MgH and AlH are, however, well known[13] to permit a comparison of this nature (Mg → MgH → Al → AlH → Si), and in Fig. 2*a*, *b* their potential gradients are drawn, combining through the normal 3^2P and the excited 4^2P states of Al. Their quantum assignments, as given in Table IV., are based on the application of the l_τ-con-

[13] The latest papers discussing new band systems in MgH and AlH are here given: R. W. B. Pearce, *Proc. Roy. Soc.*, **122**, 442, 1929; E. Bengtsson and E. Hulthén, *Z. Physik*, **52**, 275, 1928.

servation rule. The normal $^1\Sigma$-state in AlH forms a closed electronic configuration $3s\sigma^2p\sigma^2$, the stability of which we mainly attribute to the large drop of energy between Al ^2P and Si $3s^2p^2\,^3P$. The excited $^1\Pi$-level is also supposed to originate from the normal ^2P-state in Al, and is combined with the $3s^2p^2\,^1S$ term in Si. Similar relations should hold for the still higher excited levels in MgH and AlH. Our arrangement is in agreement with the spectroscopic results. Thus, the $^1\Pi \rightarrow {}^1\Sigma$ system appears strongly in emission at high pressure in the Aluminium-Hydrogen arc, while the intensity of the ultra-violet $^1\Sigma' \rightarrow {}^1\Sigma$ system gradually increases when the pressure is reduced to about 10 mm. Further, the $^1\Pi \rightarrow {}^1\Sigma$ system shows a thermal excitation in the absorption tube similar to that of gold hydride mentioned above.

TABLE IV.

	Term.	Cm.$^{-1}$.	ω_0. ω_0x.	r_0.	H — electron.	M — electrons.	Molecular State.	Combined Atoms.
MgH	$^2\Sigma$	0	1462·2 31·25	1·74	$3p\sigma$	$3s^2\,^1S$	$3s\sigma^2p\sigma$)	$3s^2p\,^2P$
	$^2\Pi$	19,271	1568·7 34·75	1·70	$3s\sigma$	$3sp\,^3P$	$3s\sigma^2p\pi$)	
	$^2\Pi'$	41,237	(1624)	1·71	$3s\sigma$	$3s4p\,^3P$	$3s\sigma^24p\pi$	$3s^24p\,^2P$
AlH	$^1\Sigma$	0	(1625·1)	1·66	$3p\sigma$	) $3s^2p\,^2P$ (	$3s\sigma^2p\sigma^2$	$3s^2p^2\,^3P$
	$^1\Pi$	23,471	(1082)	1·69	$3p\sigma$	)	($43s\sigma^2p\sigma\pi$	$3s^2p^2\,^1S$
	$^1\Sigma'$	44,597	(1326)	1·65	$3p\sigma$	$3s^24p\,^2P$	$3s\sigma^2p\sigma4p\sigma$	$3s^2p4p\,^3P$
	$^1\Sigma''$	49,290	—	1·63	$3p\sigma$	$3s^24s\,^2S$	$3s\sigma^2p\sigma4s\sigma$	$3s^2p4s\,^1P$

The excited $^1\Pi$ and $^1\Sigma''$ states (the latter not reported before) are noticeable on account of the anomalous behaviour of the intensity progression of band series related to these states. Thus the intensity of these band series is abruptly cut off at exceptionally small rotational-vibrational quantum numbers. In a forthcoming paper [1] this problem will be thoroughly discussed in relation to phenomena which appear by the interaction or near approach of potential gradients, such as those given in Fig. 2*b*.

By treating the special problem of hydride molecules, we have above mainly emphasised the influence of the mutual position of spectra terms in the separate and the combined atoms. However, as already pronounced by Hund and Mulliken, the problem of molecular states and their stability contains a number of rather incoherent moments of energy, the sum of which gives the real expression of the effect of affinity. It is to be expected that a continued development of our theoretical and empirical knowledge on band spectra will have many advantages in solving this important problem.

The authors wish to express their great indebtedness for a grant from the Nobel Foundation.

[1] E. Bengtsson and R. Rydberg, *Z. Physik* (*in press*).

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THE SPECTRA OF METAL MOLECULES.

By S. Barratt (*Chemical Department, University College, London*).

Received 30th August, 1929.

It has long been known, as the result of physico-chemical investigations, that metals and alloys in the liquid state have in general a high molecular complexity. Nothing, however, could be deduced as to the behaviour of the same symptoms in the vapour state, and so far as vapour density determinations, etc., were able to show, the vapours of the more electro-positive elements were uniformly monatomic.

A study of the absorption spectra of the same vapours has revealed that this conclusion is not strictly true, and that in many metallic vapours there must be a small proportion of di- or polyatomic molecules, for they possess well-defined, and often intensely-developed, band spectra. Perhaps the best-known examples of such spectra are those of the alkali metals and of mercury. The important suggestions made by Professor Franck at a previous meeting of the Society [1] gave a further impetus to the study of these metallic molecules. They would seem to have a very simple homopolar structure, and the original electronic configurations of the component atoms may only suffer comparatively small disturbances in their formation. In accordance with this view, many of the band spectra are closely associated with the atomic line absorption spectra; and the study of these relationships, and their explanation in terms of molecular structure, is a field of increasing interest.

It has also become evident from an examination of the absorption spectra of mixtures of metallic vapours that many such mixtures contain compound molecules (say of the type MM′ when M and M′ are two different metals), since characteristic band spectra are developed in the vapours. The total number of metal molecular spectra that becomes available for study is thus enormously increased, and it should be possible soon to accumulate sufficient experimental data for a general study of the structure and behaviour of this class of molecule. Among the spectra of these compounds, so far established, are those of the "mixed molecules" of the alkali metals (*e.g.*, NaK, LiCs, etc.), and there would seem to be a characteristic spectrum for each of the possible pairs of these metals.[2] Magnesium, in conjunction with the alkalis, yields another group of spectra.[3] The spectra of the ZnHg, and of the Cd Hg molecules have also been recognised.[4] It is proposed to describe in the present communication experiments recently undertaken from this point of view upon the vapours of mixtures of cadmium, zinc, and mercury, with those of the alkali metals. Since a series of new spectra, which is virtually a complete one, has been identified, it is evident that all these alloys must yield a certain proportion of compound molecules on vaporisation—though the absolute amount of the association is probably small.

It is not necessary to enter here into details of apparatus, especially

[1] *Trans. Faraday Soc.*, **21**, 536, 1926.
[2] *Proc. Roy. Soc.*, **119A**, 257, 1928. [3] *Ibid.*, **109A**, 194, 1925.
[4] J. G. Winans, *Physical Rev.*, **32**, 427, 1928; and *Phil. Mag.*, **7**, 565, 1929.

as these have been given in previous papers on the alkali metal spectra, but the following outline may be useful. For preliminary observations, the metals were vaporised in a steel tube electrically heated, with water-cooled end windows. This simple arrangement is easily and rapidly worked, but it has an important disadvantage when experimenting with mixtures of metals with widely-separated boiling-points. The more volatile metal is apt to distil away completely from the heated portion of the tube before the other component has given an appreciable density of vapour, so that the compound spectra do not develop, or do so only for a short time. The apparatus used in the final experiments consisted of a sealed hard-glass tube, about 9 ins. long, with the ends blown as thin and as uniform as possible, to minimise the distortion of the light beam when passing through them. This container was enclosed in an electric furnace, and had attached to it a long side-tube with an independent heating system. By placing the more volatile metal in the side-tube and the other in the main tube, it was possible to obtain a mixture of the vapours in any desired proportion by regulating the temperatures of the main and the side-tube. Such an apparatus, it is true, is not practicable for observations in the ultra-violet, but the preliminary work gave indications only of spectra in the visible region, so that the limitation was not of importance.

The alkali metals themselves, and their alloys with each other, possess extensive band spectra in the same spectral region, so that certain of these bands were necessarily present in each absorption spectrogram obtained, as well as the new spectra under discussion. Fortunately, long experience with these metals, and the wide range of comparison plates that was available, made it easy to allow for all such complications. The alkali bands could, in addition, be repressed to some extent by using large excess of the other component (Cd, Zn, or Hg). None of the metals of Group IIB., when examined alone, show absorption in this region.

The new spectra recognised in this way resemble in their general characteristics the metallic molecule spectra which have been previously examined, that is to say, they contain two distinct types of absorption: (1) Electronic band systems, showing fine structure; and (2) Isolated diffuse bands with no fine structure, which terminate abruptly on the long wave-length side and broaden, with increased density of vapour, towards the ultra-violet. In some cases, such bands are definitely the starting point of a weak continuous absorption stretching towards shorter wave-lengths. The spectra under discussion differ from those of the alkali metals in that these diffuse bands are their more prominent feature. With many pairs of metals, in fact, the diffuse bands were the only new absorptions registered on the plates, and the remaining pairs for which the ordinary type of band system was also found, gave it only weakly. The positions of the heads of the diffuse bands corresponding to the different molecules are given in the table on p. 760.

The width of these bands, when well developed, is about 20 or 30 Å. It is dependent to some extent on the density of the vapour in the absorbing column. Their appearance is quite unaffected by the presence or absence of an atmosphere of an inert gas—argon and hydrogen were both introduced on occasion. On plates secured with dense vapours it could be seen quite distinctly that the bands were the beginning of a weak continuous absorption extending indefinitely on the short wave-length side.

Only a few bands belonging to this group of molecules have been found which show fine structure. The component heads of these are much more closely packed than are those in the alkali metal band spectra, and they are unsatisfactory subjects for work under low dispersion. Observations on them are still in hand, but the details are not ready for publication. Fine structure bands have been identified only in the absorptions of "Cs Hg" (three band heads at 4991, 4984, and 4975), and of mixtures of rubidium with zinc, cadmium, and mercury. These three spectra all show characteristic bands in the region λλ4400-4200. The three systems are quite distinct, but they will require careful examination before details can be published.

	Na.	K.	Rb.	Cs.
Zn	—	4147	—	5163 5126
Cd	4000 3974	4191 4172	4487 4423	5316 5228
Hg	6499 6454 4649 4425 4406	6188 6150 4113 3988 —	6364 6335 4879 — —	5343 5222 5112 4932 4817

To summarise, the most important characteristic of this group of spectra is the uniform presence of the diffuse type of band. The same type is found in the alkali metal spectra (both of the single metals and of binary mixtures) and in the magnesium-alkali spectra. The bands are such a prominent feature of these spectra that a satisfactory explanation of them will undoubtedly afford much information about the molecules responsible for them.

The hypothesis has been advanced in a previous paper [5] that these diffuse bands represent the dissociation spectra of the corresponding molecules; or in other words that the bands are analogous in origin to the continuous absorption spectra of the halogens.

This view accounts satisfactorily for the sharp long wave-length limit of the bands, for their "degradation" towards the ultra-violet, and for the weak continuous spectra known to be associated with some of them.

It is possible to calculate, on this basis, the heat of formation of the molecules from the position of the bands—assuming, for example, that the molecule is a diatomic one, and dissociates into one normal and one excited atom. A comparison of these values with those obtained by independent methods would give a quantitative test of the hypothesis. The data required for such a comparison are available at present for the K_2 molecule alone, but there the agreement is good. Carelli and Pringsheim [6] estimate a heat of formation for this molecule of 0·51 to 0·63 volts, from observations on the intensity of fluorescence in the vapour. The value obtained from the band position—on the foregoing assumptions—is 0·53 volts.[7]

[5] *Proc. Roy. Soc.*, **119A**, 257, 1928.
[6] *Z. Physik*, 44, 643, 1927.
[7] See Ditchburn, *Proc. Roy. Soc.*, **117A**, 486, 1928.

It is unfortunate that non-spectroscopic estimates for the heats of formation of other molecules of this class are not available, to test whether this agreement is only fortuitous. If the same hypothesis is to be applied to the new spectra which have been described above, it will clearly need amplification, for each molecule gives rise not to one such band, but to several, and there are instances of two diffuse bands occurring at quite a short wave-length interval. A greater complexity in the spectrum would naturally be expected if the molecules responsible for them are more than diatomic. This is itself quite an open question, which will probably only be settled by an analysis of the fine structure bands, when these have been fully recorded. There is, at least, no doubt of the experimental fact that diffuse bands with the same general characteristics are to be found in all the known spectra of metal molecules containing an alkali metal atom. It so happens that very few metal molecules have as yet been recognised which have not an alkali as one component, and it is not possible to generalise further. There are certainly continuous absorptions of molecular origin in the cadmium and zinc spectra, but these, unlike the bands in question, broaden towards longer wave-lengths, and so cannot be regarded as analogous.

Winans [8] has suggested an ingenious explanation of the phenomena in these two spectra.

There is a further remark which it is desirable to make in connection with future work on this class of spectra—the necessity of great experimental caution in assigning observed absorption band spectra to a purely metallic origin. The great difficulty of determining the true origin of many emission band spectra is well known, but for obvious reasons the uncertainty is less when the spectra are observed in absorption, and with care a definite conclusion can usually be drawn. The sensitivity of the absorption method for the detection of certain classes of molecule is, however, extremely great and, if any of these highly absorbent molecules are present as traces in the vapour under examination, their spectra will certainly be registered and may (and have been) wrongly put to the account of the metal present in bulk.

To take an example, it has been established in this laboratory that many metals (*e.g.*, those of Groups II. and III., lead, etc.) are capable of forming, under suitable conditions, volatile subchlorides which possess strongly developed absorption spectra. Most laboratory samples of these metals contain a small amount of chloride as impurity, and if they are vaporised in the ordinary way, the subchloride bands form a prominent feature of the resulting absorption. Such bands have several times been catalogued as part of the true molecular spectra of the metals themselves. Thus, band spectra due to cadmium subchloride (Cd Cl), and to zinc subchloride (Zn Cl), have been considered part of the cadmium and zinc spectra.

Another rather interesting example of the same difficulty is afforded by a spectrum in the region λλ3200-3300, which has recently been attributed, on two separate occasions :

(*a*) To a cadmium molecule, Cd_2 ;

(*b*) To the molecule of a thallium mercury compound.

It is, however, developed much more completely in thallium chloride vapour, under conditions precluding the presence of any free metal, and is undoubtedly the absorption spectrum of this salt itself.

[8] *Phil. Mag.*, **7**, 555, 1929.

Thallium is a common impurity in cadmium, a fact which accounts for the frequent appearance of the spectrum in the vapour of commercial cadmium, since traces of chlorine are also invariably present in the metal. It is easy to devise methods which obviate these uncertainties. For example, these chloride spectra are eliminated by the addition of a small amount of an alkali metal to the vapour (potassium is a convenient metal, as its own band spectrum is not extensive), as the chlorine is removed in the form of alkali chloride. For the same reason it is always necessary to compare the spectra exhibited by the vapours of different samples of the same metal, obtained from independent sources, before reaching a safe conclusion. It would seem that a band spectrum may only be attributed to a metallic molecule after a very careful elimination of the impurity spectra which almost invariably accompany them.

VISIBLE ABSORPTION SPECTRA IN SOME CRYSTALLINE SALTS OF THE RARE EARTHS.

By F. I. G. Rawlins.

Received 26th July, 1929.

The characteristic and remarkably sharp absorption bands exhibited by certain salts of the rare earths in the visible region of the spectrum have been known for a number of years: nevertheless, a general review of the literature[1] revealed the fact that most investigators had focussed their attention more upon the mapping of the spectra (sometimes, however, only in solution) than upon an endeavour to find any guiding principle linking these particular phenomena to other, and more well-established observations in spectroscopy. A cause which has—in effect—tended to give an exaggerated importance to the study of solutions rather than of crystals is the experimental difficulty of dealing with minute samples (about 1 mm. in their longest dimension) of rare and costly material. Clearly, one cannot expect accuracy of a high order as judged by spectroscopic standards for the determination of wave lengths, yet the problem seemed of sufficient interest and importance to justify a preliminary attack with the simplest of apparatus in an attempt to bring these spectra into line—as far as may be—with the findings and demands of quantum physics. It is with this aspect of the question that the present paper is concerned.

From an experimental point of view, it may suffice to mention that the nitrate and the sulphate of the rare earths Praseodymium [Z = 59], Neodymium [Z = 60], and Samarium [Z = 62], were examined with a microscope and microspectroscope in conjunction, with the result that the main features—and many of the details—of the spectra reported by previous investigators[1] were confimred.* For the Praseodymium compounds good agreement was found with the figures due to Ephraim and Bloch.[2]

[1] Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. V.; Szivessy, *Handbuch der Physik* (*Geiger-Scheel*), Vol. XX.; Hevesy, *Die seltenen Erden*.

* The newly-discovered element Illinium (Il, Z = 61) comes into the series. Unfortunately, it has not been possible to obtain a sample.

[2] Ephraim and Bloch, *Ber.*, **61**, (1), 72, 1928;

The most striking feature is the sharpness of some of the lines: for example, two of the intense lines in the green of the Nd salts are not more than some 10 Å.U. wide, of great intensity, and closely resemble line spectra. In a word, it is the character of these crystal absorption spectra that is so remarkable. From a quantitative aspect, however, a fact emerges from which theory must start, and which forms at least a basis in the present state of knowledge. This is that (within the limits of experimental error) the spectra of the nitrate and of the sulphate of any one metal are indistinguishable from one another, though great differences exist between the spectra of these salts when the metals are interchanged. Thus, one is forced to consider the metal as in some way primarily responsible, and two main questions accordingly arise :—

(1) What exactly is the cause of these bands in the light of the facts just mentioned ?
(2) Why do these bands occur only in compounds of the rare earths ?

The answer to (1) undoubtedly lies in the ionisation in the crystal, and in the consequent production of a common cause for the spectra. Thus, if R stands for Pr, Nd, or Sm, in both the nitrate and in the sulphate we must be dealing with R^{+++} as the " carrier " of the spectrum ; the almost complete identity would seem explained on no other assumption. Very strong additional support to this comes from the spectra of these same salts in solution : the experiments of Forsling [3] and of Rech [4] give spectra very similar to those already described : it is only the weakest bands in the crystal spectra that are lacking for the solutions.

The view put forward by Ephraim and Bloch,[2] who draw a distinction of kind between the binding in $Pr_2(SO_4)_3$ and $PrCl_3$ would appear to have little to commend it. They observed the similarity between nitrate and sulphate (but only for Pr), and suggested that their spectra are similar because of the Pr—O binding, and that the halides, with complete ionisation, do not give lines identical with those of Pr—O. Two of several factors which decide against this explanation may be quoted : (*a*) the halide spectra observed by them differ amongst themselves ; and (*b*), the chloride spectra of Nd and Sm agree well with those of the other salts,[1, 3, 4] and obviously there is no choice but to attribute all to Pr^{+++}, Nd^{+++}, and Sm^{+++}.

Question (2) needs a discussion of the electronic configuration of the rare earths for its answer.

The sharpness of the absorption bands (this characteristic has been said already to resemble line spectra) is peculiar to the rare earths by virtue of an intrinsic property of rare earth atoms. The electronic arrangement in Pr, Nd, Il, Sm may be represented as follows :—

	1_1	2_{11}	2_{21}	2_{22}	3_{11}	3_{21}	3_{22}	3_{32}	3_{33}	4_{11}	4_{21}	4_{22}	4_{32}	4_{23}	4_{13}	4_{14}	5_{11}	5_{21}	5_{22}	5_{31}	6_{11}
Pr	2	2	2	4	2	2	4	4	6	2	2	4	4	6	1	–	2	2	4	1	2
Nd	2	2	2	4	2	2	4	4	6	2	2	4	4	6	2	–	2	2	4	1	2
Il	2	2	2	4	2	2	4	4	6	2	2	4	4	6	3	–	2	2	4	1	2
Sm	2	2	2	4	2	2	4	4	6	2	2	4	4	6	4	–	2	2	4	1	2

The introduction of the 5_{31} electron starts with Lanthanum, the ground term of which is a ^2D state ; hence it is assumed that the 5_{31} electron acts as the " spectroscopic " electron. Likewise, in neutral Pr, Nd, Il,

[3] Forsling, *Bihang. Svenska Handl.*, **18**, 4, 10, 1893.
[4] Rech, *Z. wiss. Photochem.*, **3**, 411, 1905.

Sm the " spectroscopic " electrons are almost certainly 4_{43} and 5_{31}, and thus we have for the four elements

	"Spectroscopic" electron. 4_{43}.	5_{31}.	Multiplicity $(2s + 1)$.
Pr	1	1	3
Nd	2	1	4
Il	3	1	5
Sm	4	1	6

an arrangement which is generally accepted.

Ionisation, either in the crystal or in solution, removes the 6_{11} and 5_{31} electrons, but leaves the 4_{43} electrons, which are of similar energy content.

External fields may be expected to have little effect upon these 4_{43} electrons, for they are well shielded by the 5_1 and 5_2 shell: as a direct consequence they still behave as " spectroscopic " electrons, and are responsible for the sharp absorption spectra both in crystal and solution, and also the line emission spectra of the oxides, when the 5_3 and 6_{11} electrons are bound in chemical combination, but in which the 4_{33} electrons are still available for spectroscopic purposes.

The ground states of the ions may be expressed :—

	Multiplicity.
Pr^{+++}	2
Nd^{+++}	3
Il^{+++}	4
Sm^{+++}	5

and naturally will have little relation to the arc spectra of the neutral atoms.†

It is then the incompleteness of the inner shell which gives the rare earths this property, as well as many another.

There remains the pleasant task of making a number of grateful acknowledgments.

Professor A. Hutchinson, F.R S., has provided facilities within his department for carrying out the experiments, and to him the author would like to express his best thanks, as also to Professor Sir William Pope, F.R.S., for the loan of material. Mr. C. P. Snow has been associated with the work throughout, and his knowledge of spectroscopy has proved invaluable. In fact, it is difficult to see how this paper would ever have reached its present state without his help and suggestiveness: to him, therefore, the author's obligations are great. Dr. F. L. Gilbert kindly undertook the preparation of several of the salts. It is a pleasure to acknowledge very cordially his skilful co-operation in this respect.

Summary.

The visible absorption spectra of the crystalline nitrates and sulphates of Pr, Nd, and Sm are ascribed to the ions Pr^{+++}, Nd^{+++}, and Sm^{+++} as " carriers."

The noteworthy sharpness of many of the lines is due to the shielding of the 4_{43} electrons by the 5_1 and 5_2 shells.

† Comparison with the data, though not of recent origin, tabulated in Vol. V. of the *International Critical Tables*, generally speaking, bears this out.

These spectra are peculiar to the rare earths on account of the incomplete nature of their inner electronic shells.

From a consideration of the ground states of the ions R^{+++}, it is not to be anticipated that any obvious relation will exist with the spectra of the neutral (metal) atoms.

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Cambridge.

ABSORPTION SPECTRA OF POLYATOMIC MOLECULES.

Predissociation and Dissociation of these Molecules.

By Professor Victor Henri (*Zürich*).

Communicated to the Society on 24th September, 1929.

The study of the absorption spectrum is much more complicated in the case of polyatomic molecules than in that of diatomic; it is in fact not possible to give a complete analysis of the electronic configurations for a molecule formed by more than two atoms. Any state would be represented by about one hundred or more letters.

For the vibration spectra also, the complete solution of the problem is complicated by the mutual influence of different vibrations. But, in this case, we can now obtain for several spectra an approximate representation of the vibration spectra.

Generally, we may observe that, for complicated molecules like benzene and derivatives, the vibrations are very nearly harmonics; the correction for non-harmonicity is very small.

The formula of the vibration spectrum can be represented at a first approximation by the formula :

$$\nu = \nu_0 + p'\alpha'(1 - x'p') + q'\beta'(1 - y'q') + r'\gamma'(1 - z' \,.\, r') + \ldots$$
$$- p_0\alpha_0(1 - x_0p_0) - q_0\beta_0(1 - \gamma_0q_0) - r_0\gamma_0(1 - z_0r_0) - \ldots$$

In this formula α', α_0, β', β_0, γ', γ_0, . . . are the different vibration frequencies in the activated and normal molecule, and p', p_0, q', q_0, r', r_0 . . . are the corresponding vibration quantum numbers.

By studying the absorption spectrum of a great number of different molecules (more than 40), we have found that there is a common feature in the structure of the spectrum, which in every case appears on the ultra-violet side of the spectrum. Those bands which for lower frequencies have a fine structure with quite definite edges and sometimes a well-developed rotation spectrum, become for higher frequencies broad, diffuse; the edges are not very sharp and there are no more rotation lines.

As an example, there is given in Fig. 1 the absorption spectrum in the far ultra-violet of NO_2 vapour; the photographic reproduction shows first, two vibration bands $\lambda = 2491$ and 2459 with many very fine rotation lines, which correspond to a double rotation of this triangular molecule, that we have studied with Louis Harris. There are similar bands with fine structure towards the visible corresponding to different vibration states of the molecule. But the next bands towards the ultra-violet

side change abruptly in their structure ; this is quite visible for the bands 2447 and 2425, and there are about ten bands of this sort in the far ultra-violet.

The upper microphotometric registration shows very clearly the abrupt change in the structure of the bands.

The bands are diffuse, without any fine structure ; the quantisation of the rotation movements of the molecule has disappeared totally, but the vibrations are quantised : the bands are distributed at nearly regular intervals.

A second example is that of sulphur vapour, S_2, given in Figs. 2 and 3. The vapour was at the temperature of 600° C. One-tenth of milligram of sulphur is enclosed in a quartz tube of volume 16 c.c. and length 10 cm. In this condition, the vapour consists practically of S_2 molecules. There is a series of about 20 vibration bands with a period of 397 cm.$^{-1}$ in the first part and of 365 to 350 cm.$^{-1}$ in the second ultra-violet part. These bands are formed by a large number of fine rotation lines (Fig. 3 to the left).

But exactly at the limit 2792 Å., all fine structure disappears suddenly and the bands are then diffuse with only vibration bands without any rotation line.

The photomicrograph of Fig. 3 shows this abrupt change in the absorption spectrum. There are two curves corresponding to two different points of the same spectrum ; and the third lowest curve corresponds to the iron spark.

In Fig. 2, the absorption spectrum is given with less enlargement, so that one can see twelve successive vibration bands, as well as the two limits of predissociation. The same result is obtained for many other substances.

The physical signification of this modification in the absorption spectrum of any substance in vapour state could be analysed by different investigations.

We found following the general results for the properties of the molecule in the region of broad diffuse bands :—

(1) The vibration frequency in this region decreases, indicating an increase in the distance between the vibrating masses—the molecule becomes *labile*.

(2) The fluorescence excited by the light in the region of the diffuse bands is very feeble, or, indeed, entirely absent.

(3) The molecule becomes chemically active in this region of spectrum.

(4) The limit of the production of diffuse bands is displaced towards the red by raising of the temperature. This displacement is larger for substances with high molecular specific heat, than for those with low specific heat.

These results indicate a new state of the molecule, which is preparatory to the dissociation and we called it the "*predissociation of the molecule.*"[1]

We are able to study this special chemical activity of the molecules in the region of diffuse bands by two examples. These are the photochemical decomposition by monochromatic light of benzaldehyde vapour, in which case we obtain quantitatively benzene and carbon monoxide :

$$C_6H_5COH \rightarrow C_6H_6 + CO,$$

[1] *Nature*, December 20, 1924.

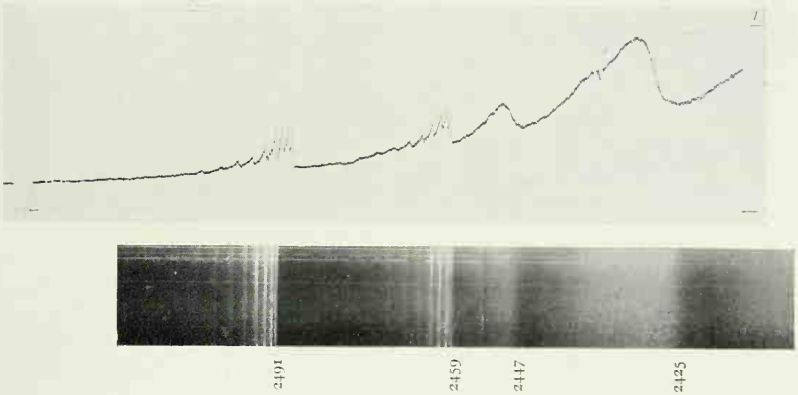

FIG. 1.—NO_2 vap. Reserv. − 31°. tube + 130°. $d_1 = .200$ mm.

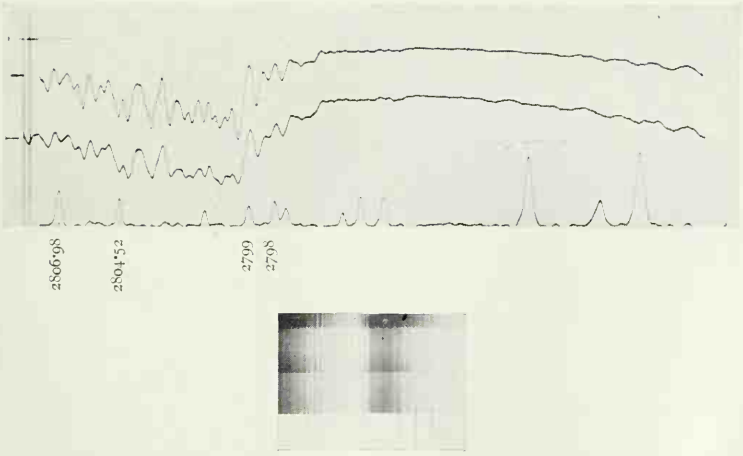

FIG. 3.—S_2 vap. (1) Predissociation. $t = 600°$.

[*To face page* 766.

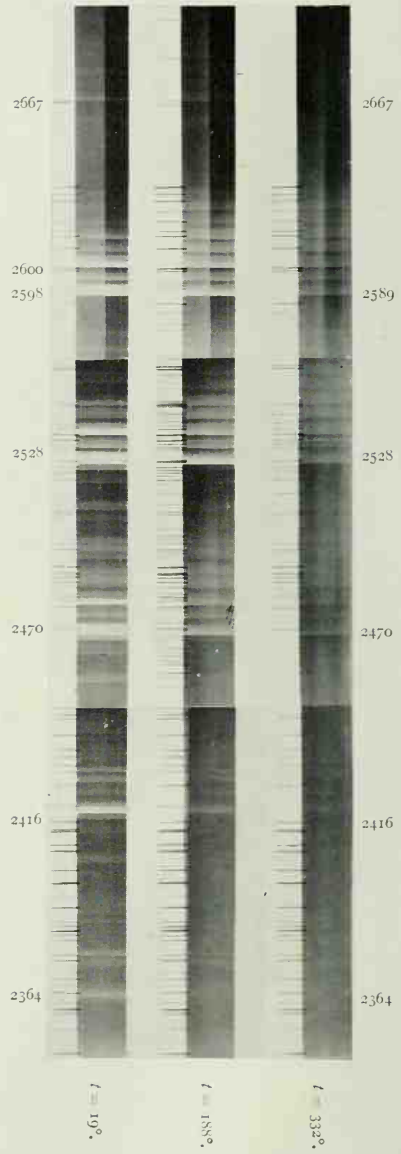

FIG. 6.—C_6H_6 abs. vap. $p = 5$ mm. $d = 30$ cm.

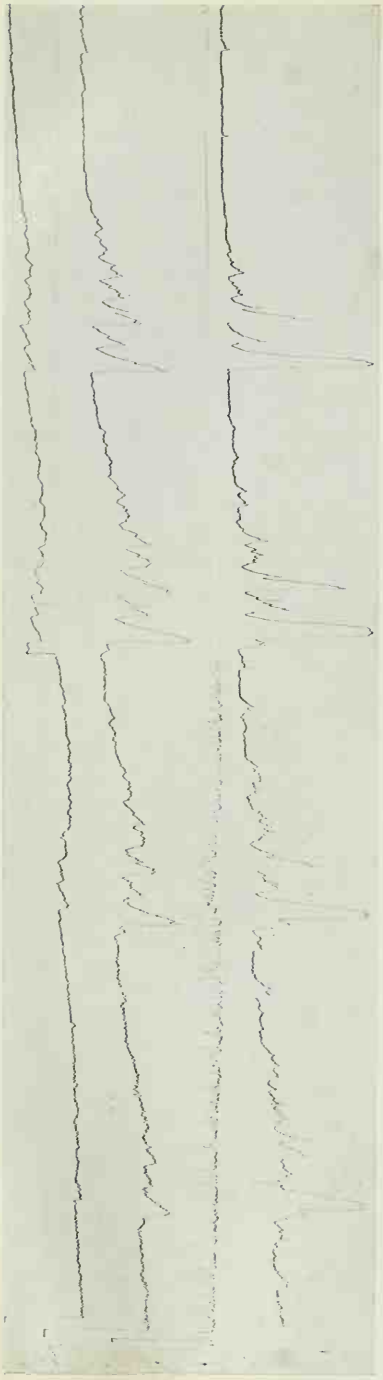

FIG. 7.—C_6H_6 vap. abs. $p = 5$ mm. $d = 30$ cm.

and the photochemical dissociation of acetaldehyde :

$$CH_3COH \rightarrow CH_4 + CO.$$

The first reaction was studied in my laboratory by M. de Hemptinne, and the second by James H. C. Smith. It was found that, in both cases, only light corresponding to the region of diffuse bands produces the dissociation of the molecule. The light from regions where the absorption bands have a fine structure has no action on these molecules.

But, when the vapour of benzaldehyde or acetaldehyde is heated to 200° C., the absorption spectrum changes. Thus, for benzaldehyde, the diffuse bands appear for $\lambda = 2750$ Å. at 200°, and only at 2550 Å. for 20°, and for acetaldehyde, the diffuse bands appear at 3200 Å. at 200°, and at 3050 Å. at room temperature. At the temperature of 200°, the photochemical dissociation is produced for benzaldehyde by rays of $\lambda = 2750$ and for acetaldehyde of $\lambda = 3200$ instead of $\lambda = 2550$ and 3000 at the temperature of 20°.

There is an exact parallelism between the structure of the absorption spectrum and the chemical activity of the molecules.

This change of the absorption spectrum with increase of temperature is a general result, which I studied especially with MM. de Hemptine and Almasy.

We give in Figs. 4, 5, 6, and 7 examples for the absorption spectrum of benzene vapour at different temperatures.

Fig. 4 corresponds to C_6H_6 at $p = 5$ mm., the tube length being 30 cm. The quartz tube was sealed and the absorption spectrum photographed at $t = 18°$, then 325°, then 18°.

In Fig. 5 are given the absorption spectra at 18° and 325° with greater enlargement.

In Fig. 6 are three spectra at 19°, 188° and 332°.

And in Fig. 7 are photomicrographs of the absorption spectra given on Fig. 6.

We see, for example, in Fig. 6 that the temperature produces a change in the absorption spectrum. The bands are broadened and become diffuse. This influence of temperature begins on the ultra-violet side and progresses more and more towards the red by increase of temperature.

We see that the heating of any substance produces a predissociation of the molecules ; we call this effect "*thermal predissociation*". There is an exact addition of thermal energy and light energy.

This result shows that increase of temperature has an effect on the stability of the molecule ; the vibrations of the atoms are enhanced and the distances are increased. It gives an analysis of the influence of temperature on the velocity of chemical reactions.

We can directly see by studying the absorption spectrum that the temperature effect consists not only in the enhancement of the kinetic energy of the molecules, but also in the modification of the internal energy, which is followed by alteration in the internal structure of the molecules, the distances between different atoms being increased.

This temperature influence is especially high for molecules with great molecular specific heat, where we have a large number of degrees of freedom. It is, moreover, possible by the displacement of the predissociation limit corresponding to an elevation of 100° or 200°, to calculate the value of the molecular specific heat of the substance.

GENERAL DISCUSSION

BAND SPECTRA IN VISIBLE AND ULTRA-VIOLET.

Professor J. Errera (*Brussels*), with reference to the Introductory Paper asked how it was possible to reconcile the statement that HCl is homopolar with the fact that its permanent electric moment is very high, in view of the fact that the elements constituting the molecule should be in the ionic state and not neutral atoms. It would be interesting to know the electric moments of the different salts NaCl etc. in the vapour phase; the investigation had been started in his laboratory.

The high voltage necessary for the dissociation of HCl might perhaps be associated with questions as to the relative diameters of the elements constituting the molecule.

Professor Lennard-Jones (*Bristol*) said: The question raised by Professor Errera is largely one of notation. If *homopolar* molecules are defined (after Franck) as those which separate adiabatically from the ground state into atoms and *heteropolar* those which separate into ions, then HCl may certainly be described as homopolar.

Dr. G. H. Dieke (*Groningen*) referring to Professor Richardson's paper on nomenclature, said that practical workers required a simple notation with fewer symbols than were needed by theoretical workers. He personally disliked equations in which all the letters were capitals, as would be introduced by Professor Mulliken's systematic notation. Again, confusion might easily arise if the same letter n remained in use for both the principal electronic quantum and the vibrational quantum number; he therefore suggested that n be retained for the former (as in atomic line spectra) and v be used for the latter.

Dr. W. Jevons (*London*), said: In my reply to Professor Mulliken's letter inviting expressions of opinion, I suggested that V would be far preferable to n for the vibrational quantum number, in view of the wide use of n for the principle quantum number. Although I mentioned the capital V in order to conform with the proposed J, M, and N, I would be equally content with the small v just suggested by Dr. Dieke. I also stated that if another symbol would be preferable to J, I saw no reason why the change should not be made, provided that it (as well as the substitution of v for n) is made at the same time as all the other changes indicated in the paper. The points in the new notation which I especially welcome are (i) the use of the subscript e to distinguish the equilibrium positions of the nuclei, from the $n = 0$ vibrational state, and (ii) the abolition of the sub-subscript as in i_{l_τ}.

Professor Mecke (*Bonn*), said: I entirely agree with Dr. Dieke. For practical work (the analysis of band spectra) we must choose a notation as simple as possible; for theoretical problems (determining the different electronic levels and their properties) I think it will never be possible to adopt a uniform notation accepted by every one. I am told that the proposed notation has already been changed again and in the near future this will be the case with every other notation. Theorists wish to express too many things with a few signs and symbols; this is not good, for the notation will be altered as soon as the theory is changed—we have seen in the last two or three years how often these theories have changed. For this reason I think it will be better *not* to accept a uniform notation but, rather, to suggest that each author should make—before starting his work—a list of symbols and characters to be used and put this list at the beginning of his paper; of course he should be urged to keep as closely as possible to the proposed

notation. For practical work I should prefer a notation which has been accepted by many authors for several years rather than to make such changes of principle as have been proposed; this will give rise to more confusion.

I would suggest the following simple notation :—

(1) Take n as the quantum number of vibration (whole number) and use a formula like $\nu = \nu_0 + (a'n' - b'n'^2) - (a''n'' - b''n''^2)$ or $\nu = \nu_0 + \omega_0'(n' + \frac{1}{2}) - \omega_0'x'(n' + \frac{1}{2})^2 - \omega_0''(n'' + \frac{1}{2}) + \omega''x''(n'' + \frac{1}{2})^2$ for the different bands of a system. In order to denote a certain band of the system always put the vibrational quantum numbers in parenthesis : (1, 0) means $n' = 1$, and $n'' = 0$. In the case of polyatomic molecules use subscripts to the constants of the same character (a_1, a_2, a_3 or ω_1, ω_2, ω_3 for the different vibration frequencies) but use n, p, q, r . . . for the corresponding quantum numbers.

(2) Always take primed letters (′) and symbols to denote the higher levels and double primed (″) letters for the lower levels but avoid speaking of the initial and the final state, since in absorption the initial state is the lower and in emission the higher one.

(3) The pure rotation terms should be denoted by $F(j)$ or $F(m)$, m and j being the numbers of the lines in the different branches. j should be equal to the total angular momentum, m to the angular momentum round an axis perpendicular to the axis of the molecule. For unsymmetrical molecules a third rotation number k might be necessary.

(4) The different branches of the band should be called $O(j)$, $P(j)$, $Q(j)$, $R(j)$ and $S(j)$ corresponding to the changes $j' = j'' - 2$, $j' = j'' - 1$, $j' = j''$, $j' = j'' + 1$ and $j' = j'' + 2$, analogous to the changes of m and k in the case of polyatomic molecules.

(5) The following symbols are well known : $B = h/8\pi^2\mathrm{I}$, $\mathrm{I} = \mu r^2 =$ moment of inertia, $r =$ the distance between the nuclei, $\mu =$ the reduced mass. $B_n = B_0 - \alpha n$. Subscripts mean the value for the different vibration states (B_0, I_0, r_0 the values for $n = 0$). It is *not* necessary to distinguish between the values for $n = 0$ and those with the vibrational energy equal to zero ($n = -\frac{1}{2}$) for the latter will never be realised, the normal state of the molecule being always given by $n = 0$. Do not use D as the coefficient of j^4, as Mulliken suggests, for it might give rise to confusion with the dissociation energy. Use $B_n u^2$ as before.

In the case of polyatomic molecules it is advisable to take $I_1 \leqq \mathrm{I}_2 \leqq I_3$ for the three moments of inertia.

(6) $D =$ the energy of dissociation into *normal* atoms. In the case of polyatomic molecules D should always denote the binding energy of one single atom to the compound. An index indicates the atom meant, for example $D_{\mathrm{H}} =$ the binding energy of *one* hydrogen atom in a hydrocarbon compound (CH_4).

(7) If the electronic states are known, it will be sufficient to use the capital Greek letters Σ, Π, Δ to indicate the resultant orbital momentum around the molecular axis. Also add the multiplicity in the ordinary way ($^1\Sigma$ or $^2\Sigma$ . . .). If, in addition to this notation, it is desirable to notify the levels of the individual electrons ($1s\sigma$, $2p\pi$), the author should first explain his notation. It is preferable to use no special letter for the principal quantum number of the electronic state, but to put the number before the symbol of the Term (1Σ, 2Σ . . .). Confusion with the vibration quantum number n will be avoided in this way. The fact that the electronic states are negative should always be notified; so that the first symbol in the expression

for the frequency ($\nu = {}^2\Sigma - {}^2\Pi$) denotes the lower, the second the higher state. In the case of rotation and vibration levels the terms are positive, so that the states are reversed.

I think that this simple nomenclature will be sufficient for most purposes. It should always be remembered that papers on band-spectra are to be read not only by theorists who are used to a complicated nomenclature, but also by experimental physicists and especially by chemists. Complicated notations will never lead to the understanding of a paper.

Professor Victor Henri (*Zürich*), said: In discussing the nomenclature of band spectra, it is usual to have regard solely to diatomic molecules. One ought to think also of polyatomic molecules. In that case there would be several vibration frequencies and several vibration quantum numbers. It seems to me that the employment of n', n'' . . . for the vibration quanta leads to no advantage by reason of the confusion which is possible with the total electronic quantum. The term n should be reserved for electronic quanta and the vibration quanta should be designated p, q, r . . . In the same way in the case of the frequencies, instead of ω, one should take the letters α, β, γ . . . for the different vibration frequencies in a molecule. This is the nomenclature I use for the spectra of polyatomic molecules.

With regard to the complete representation of the electronic state of a molecule which has been proposed by Mulliken, Hund, and Richardson, I am of the same mind as Dieke. I believe that in the majority of cases this representation is too premature, and moreover the representation of the state of a diatomic molecule by 10 or 15 letters is too complicated and inconvenient from the practical point of view. It is necessary to introduce symbols which are simpler and more practical, so that by the formula one can give expression to the structure of a band spectrum.

Professor O. S. Duffendack * (*University of Michigan*), said: I hope that one of the results of this meeting will be the general adoption by writers on band spectra of a common terminology and symbolism. For one whose work leads him to make occasional excursions into band spectra regions, it is very inconvenient to acquaint oneself with the symbolism of different writers. One appreciates, of course, that at present no system can be proposed that will suffice to express all the details of analysis of a complex spectrum of a polyatomic molecule. But a large number of spectra can be described and a good many molecular quantities can be expressed by the use of symbols such as those proposed in Professor Richardson's paper. A system like that commends itself to me because of its very obvious similarity to that generally used by writers on line spectra. This similarity would make it rather easy for those familiar with the literature of line spectra to read papers on band spectra.

Professor Mulliken (*Chicago*) wrote: I should like to make some comments on the problem of band spectrum nomenclature. First, it seems desirable to point out that the suggested revised scheme of notation, which was presented to the meeting by Professor Richardson,† was in a somewhat incomplete and preliminary form, and consequently should not be taken as representing in all points a definite recommendation. In such a preliminary form it was sent out by the writer (as a

* John Simon Guggenheim Memorial Fellow.

† See page 686.

circular letter) for criticism and suggestions. It is expected that the final recommended scheme will be published later.

In view of opinions expressed by a number of people, it would seem wise to recommend the use of v in place of n for the vibrational quantum number.

In accordance with suggestions of several people, it appears desirable to recommend the use of a superscript number following the electronic term symbol, as in ${}^3\Sigma^1$, ${}^2\Pi^3_{\frac{1}{2}}$, to indicate the vibrational quantum number. [The suggestion made earlier, of giving both v and K or J in parentheses, as in ${}^3\Sigma(1, 10)$, has not met with favour.] Naturally, this can be omitted if one is interested only in the electronic state. Or if one wishes to denote also a definite state of rotation, the value of the rotational quantum number (K or J) can be added in parentheses, as in ${}^2\Sigma^0(10)$ or ${}^3\Pi^4_2(17)$. Such a designation can be preceded, if desired, by a configuration symbol, or other identifying designation, as for example $A\,{}^2\Pi^2_{1\frac{1}{2}}(7\frac{1}{2})$ or $A\,{}^2\Pi^2_{\frac{3}{2}}(7\frac{1}{2})$, or $1s\sigma^2 2p\sigma 2s\sigma$, ${}^1\Sigma^2(8)$; or if the meaning is clear from the context, this last might be briefly written $2s\sigma$, ${}^1\Sigma^2(8)$ or $2\,{}^1\Sigma^2(8)$. The methods of designation just mentioned involve a degree of standardisation suited to minimise confusion, yet permit of adaptation in a readily understood manner to suit the needs of individual cases.—No provision has been made in the above designations for denoting odd and even terms (homopolar molecules only), or positive and negative terms (these take the place of the old A and B sublevels in Λ-type doubling [formerly, but less appropriately, called σ-type doubling]). Perhaps it is best to leave the designation of these properties for the time being to individual choice, with merely the general suggestion that they be indicated by additional subscripts or superscripts (in the form of + and − signs, or of letters) on the right of the electronic term symbol. This may sometimes cause an excessive number of subscripts or superscripts, but ordinarily in practice only a part of these will be used at once. The use of a prime (′) in Wigner and Witmer's distinction between Σ and Σ' terms seems rather undesirable, because of its possible confusion with other uses of the prime.—In the designations given above, no provision has been made for giving both K and J in cases (as Hund's case b) where both are important. Perhaps this had best be left open for the present. One might use a designation such as ${}^2\Sigma^0(9, 9\frac{1}{2})$ for $K = 9$, $J = 9\frac{1}{2}$; or ${}^3\Pi^1(14, 15)$ for case b ${}^3\Pi$ with $K = 14$, $J = 15$. Or one might use designations like ${}^2\Sigma^0(9^{+\frac{1}{2}})$ or ${}^2\Sigma^0(9^+)$ and ${}^3\Pi^1(14^{+1})$ or ${}^3\Pi^1(14^+)$.

Dieke, Mecke, and Henri have suggested the use of a simplified notation for experimentalists, especially in the designation of electronic states. Clearly, such brief designations as $A\,{}^1\Sigma$ or $N\,{}^2\Pi$, or even just A or N, are sensible for referring to electronic states, in cases where there is no point in specifying the complete electron configuration, or in cases where the latter is uncertain or unknown. Also, more generally, in cases where the correct theoretical designations of energy levels, or of spectrum lines, cannot be determined, it is obviously necessary for the experimentalist to introduce (temporarily, one hopes) other designations. But it seems to me that in so far as, or so soon as, band lines and molecular energy levels can be classified on a theoretical basis, everyone should try to use designations in agreement with a uniform system.

For designating a transition between two electron states, it would seem wise to use always such a form as ${}^2\Pi \rightarrow {}^2\Sigma$ rather than the equivalent form ${}^2\Sigma - {}^2\Pi$ which is based on the old atomic symbolism (*e.g.* $1s - 2p$).

The latter is really sensible only in case each symbol corresponds to a definite term value which is a member of a series converging to a limit. Except in H_2 and He_2, such series are not known for molecular terms, and the use of the corresponding notation has no point. Even for such cases and even for atoms with series spectra, but certainly for ordinary molecular levels and for atomic levels in complex atoms, designations such as ${}^2\Pi \rightarrow {}^2\Sigma$ and ${}^2P \rightarrow {}^2S$ seem advisable, because of their intelligibility.

The designations O, P, Q, R, S can conveniently be used to denote either the value of ΔJ or that of ΔK in a band-line series, or even of both these quantities simultaneously. For example, in cases where K is the important rotational quantum number and J is of negligible importance (H_2, He_2 states, also ${}^2\Sigma \rightarrow {}^2\Sigma$ transitions with negligible doublet separations), one naturally understands by P, Q, or R branches, branches for which $\Delta K = -1$, 0 or $+1$ respectively. If, however, one can assign J as well as K values, then one may speak of for example ${}^PQ$ branches to designate $\Delta K = -1$ and $\Delta J = 0$, indicating ΔK in the superscript. Except in H_2 and He_2 and in Σ states, J is usually the important quantum number, while K is of subsidiary importance or even is lacking in significance. In some cases (*e.g.*, ${}^2\Pi \rightarrow {}^2\Sigma$ transitions with Hund's case *a* for the ${}^2\Pi$ state), designations for both ΔJ and ΔK are very desirable, as ${}^SR$, ${}^PQ$, ${}^OP$, etc.—One might suppose that the use of O, P, Q, R, and S in two different ways, *i.e.* for indicating ΔK as well as ΔJ, would lead to confusion. But I think that those who are familiar with the analysis of band spectra will agree that in practice this is not a serious danger, provided everyone merely uses O, P, Q, R, S in the manner most suited to the case in hand.

Several people have urged that Σ is after all preferable to X as the quantum number representing the projection of S on the electric axis of the molecule in Hund's case *a*. The principal arguments for Σ are: (1) the analogy L, Λ is carried on by S, Σ and is an important aid to the memory; (2) Σ is obviously a Greek letter, whereas X (Greek) is likely to become X (English) through misunderstanding by the uninitiated. It seems to me that it would on the whole be best to recommend Σ instead of X, in spite of the objections which exist to its use. I should be glad to learn as soon as possible the opinions of others on this point, and on those discussed above.

Dr. G. Herzberg (*Bristol*) said: I would like to discuss the difficulties mentioned by Professor Mulliken * a little further. It was pointed out in a recent paper by Dr. Heitler and myself that a ${}^1\Sigma_+$ state results from the individual normal atoms in the case of N_2 as well as in the case of H_2. This follows from the theory of Wigner and Witmer without any assumption as to the detailed electronic structure of these molecules. Therefore, from the experimental results of Rasetti on the Raman effect of N_2, which show that the even rotational levels are the stronger in contrast to hydrogen, where the odd rotational levels are the stronger we conclude that while ψ is anti-symmetric in the nuclei (*An* N), in H_2 it is always symmetric in the nuclei (*Sy* N) in the case of N_2. This means that the Nitrogen nuclei follow the Bose statistics, whereas, as pointed out by Mulliken, it was generally expected that they would follow the Fermi statistics (*An* N) because they contain an odd number

* See page 634.

of particles which follow the Fermi statistics. I believe that our conclusion rests on a rather better foundation than that of Mulliken, because it is based entirely on the purely group theoretical considerations of Wigner and Witmer, and not on any assumption about the detailed electronic structure of molecules. Moreover, in contrast to Mulliken's electronic structure, these same considerations lead to the observed character of symmetry for the ground state of O_2 : $^3\Sigma_-$ or $^3\Sigma'_+$.[1] We conclude, therefore, that in the nucleus the electron loses not only its spin, as shown by Kronig, but also with it its determining influence on the statistics which the whole particle obeys.[2] This seems to be very remarkable.

Dr. W. Jevons (*London*), said: The electron structure given in Table II. of Professor Lennard-Jones' paper * for the ground state of C_2 differs from that predicted by Mulliken,[3] according to whom the ground and first excited states are both $^3\Pi$ and are the two states involved in the production of the Swan system. Professor Lennard-Jones gives $^1\Sigma$ for the ground state, and accordingly, the Swan system must arise in a transition between two of the excited states, for which Professor Lennard-Jones gives $^3\Pi$. Now in stellar spectra of the low-temperature types R and N, the Swan system occurs, but (so far as I know) the other system of C_2, namely the high-pressure system, does not. Unless the conditions in the atmospheres of these stars are such that C_2 molecules can, and do, exist in at least two excited states as well as in the ground state, it would appear that the absorption of the Swan bands must arise in a transition from the ground (not from an excited) state to an excited state. I understand that such considerations of the M type stars have been adduced as evidence that the ground state of the TiO molecule is the lower $^3\Pi$ state for the " Antarian " TiO system ($^3\Pi \rightarrow {}^3\Pi$) which characterises those stars, and I wonder whether enough is known about the R and N types to permit of a discussion of C_2 from this point of view.

Professor Lennard-Jones (*Bristol*) said: If the energy difference between the $^1\Sigma$ ground state and the lowest $^3\Pi$ state of C_2 is not large, then there is a high statistical probability that C_2 molecules in stellar atmospheres are in the $^3\Pi$ state due to thermal agitation. They may then be further excited to another $^3\Pi$ level by absorption of radiation giving the Swan absorption bands.

Transitions between singlet states and triplet states are not likely to occur on absorption and, if they did, the absorption bands due to the transition $^1\Sigma$ (ground state) to $^3\Pi$ (lowest excited state) would probably be in the infra-red. A $^1\Sigma_+$ term can only combine with a singlet term of opposite symmetry, and the lowest of such levels may be so high that the corresponding absorption bands would not be observed in stellar spectra. I do not think, therefore, that the evidence from this source need be conclusive.

Mr. C. P. Snow (*Cambridge*), said: From recent observations on the vibration-rotation bands of CO it seems possible to decide between the alternative suggestions of $^1\Sigma$ and $^5\Sigma$ as the ground state of the molecule. If the state were $^5\Sigma$, the vibration frequencies of the multiplets would be expected not to coincide directly, and accordingly

[1] G. Herzberg, *Z. physik. Chem.*, **B4**, 223, 1929.

[2] For a more complete discussion of this matter, see W. Heitler and G. Herzberg, *Naturw.*, **17**, 673, 1929.

* See page 668.

[3] *Physical Rev.*, **32**, 206, 1928.

the vibration bands of the five states would overlap and give an irregular composite band. There is no sign of this complexity; Dr. Johnson's conclusion * that the ground state is $^1\Sigma$ is given strong support.

Professor H. G. Grimm (*Ludwigshafen*), referring to Mr. Johnson's paper, said: Langmuir is known to have brought the special similarity of the physical properties of CO and N_2 into relation with the isosterism of these molecules. I should like to ask whether the band-spectra of these molecules, too, would show similar features.

Dr. G. Herzberg (*Bristol*) said: In regard to the remark of Mr. Snow I should like to emphasise that a $^5\Sigma$ state does not give any splitting except in the higher rotational levels as in all Σ states and even then it is very small, *e.g.* $^3\Sigma$ of O_2 and $^2\Sigma$ of CN. It is clearly impossible to resolve this fine structure in infra-red work. But the fact that $^1\Sigma$ and not $^5\Sigma$ is the ground state of CO is proved by the diamagnetism of CO. If $^5\Sigma$ were the ground state, CO would be strongly paramagnetic like O_2.

Replying to the question of Professor Grimm, Dr. Herzberg said: According to spectroscopic and other data, the normal states of the CO and N_2 molecules are the same ($^1\Sigma$), in agreement with the fact that according to Mulliken and Hund they have the same detailed electronic structure. It is, therefore, to be expected that both molecules will have quite similar physical properties, in accordance with the facts as pointed out by Professor Grimm. Moreover, in a forthcoming paper in the *Z. Physik*, **51**, 601, 1929, I show that CO has three pairs of binding electrons (just as N_2) in accordance with the values of the heats of dissociation of these molecules, which in both cases are rather large (10 and 9 volts respectively). Brüche came to the same conclusion on account of the striking similarity between the curves for the effective cross-section of these molecules for collisions with slow electrons. This last fact also shows the similarity of the electron structure of N_2 and CO.

The purpose of the paper already mentioned was to explain the intersection of the potential curves of CN and N_2^+ and some other similar results, which are either unexplained by the Mulliken-Hund theory or even contrary to it. The intersections can be explained by assuming that in the transition from the individual atoms to the molecule all the quantum numbers of all electron shells are preserved. Thus, in altering the nuclear distance only the order of the energy of the levels is altered. It is, therefore, now possible to make definite statements about the relative position of the numerous molecular terms which, according to Wigner and Witmer, arise from two definite terms of the separated atoms, and also about the stability of these terms. No definite conclusions about these two questions could be obtained by Wigner and Witmer, or by Mulliken and Hund. Moreover, it is possible to retain the Heitler-London-Lewis conception of binding electron pairs, which was not intelligible according to Mulliken and Hund. All the experimental facts, as far as they are known, especially the above-mentioned intersections of terms, seem to be in accordance with this theory.

Dr. R. C. Johnson (*London*), in reply to Professor Grimm's question, said: It is generally agreed that the structure of the molecules CO and N_2 is the same in the ground state. The present evidence from band spectra is, however, that some at least of the excited states of the CO molecule are different from those of N_2. The quintet levels of CO have no counterpart in N_2 and the triplet levels of the latter molecule appear

* See page 649.

to be without their analogues in the former. Subsequent investigation may prove that this divergence in the structures of these two excited molecules is not so wide as would appear : at present we can only record these marked differences, for which it seems difficult to suggest any explanation.

Dr. W. Jevons (*London*), said : The spectrum of BeO for which Dr. Johnson gives predicted molecular states in Table III. is more interesting than would appear from the remark that only one band-system of the molecule is known, namely the visible system $^1\Sigma \rightarrow {}^1\Sigma$. Actually a second system is known ; it is a fairly strong ultra-violet system which, as Bengtsson [4] and I,[5] independently, observed last year, occurs with the visible system. I was inclined to ascribe it to the oxide, but did not quite exclude the possibility that it might be due to a fluoride. Bengtsson appears to have got the system with less confusion by other bands, and has represented it by $\nu_{\text{R head}} = 31899 + 1006n' - 10n'^2 - 1126n'' + 10n''^2$ (n', $n'' = 0$, 1, 2 . . .). It has no state in common with the visible system but appears to have the same band-structure (one R and one P branch). Bengtsson tentatively ascribes it also to $\Sigma \rightarrow \Sigma$. There are other bands observed by both of us in the same region, and Bengtsson suggests that they belong to a $\Sigma \rightarrow \Pi$ system. Thus, there are four, five, or six observed levels of BeO, and not only two $^1\Sigma$ levels.

Dr. G. Herzberg (*Bristol*), referring to the paper of Dr. Johnson, said : In my paper already mentioned, I have pointed out that it seems very probable that the normal state $^1\Sigma$ of BeO dissociates into one normal O-atom and one excited Be-atom in the first triplet state (^3P), whereas the excited $^1\Sigma$ level dissociates into a normal O-atom and a ^3S Be-atom. The extrapolated values of the heats of dissociation fit very well with this assumption. Moreover, on theoretical grounds it seems very improbable that the normal ^1S state of Be gives any chemical binding as assumed by Dr. Johnson because all shells are closed as in helium. This is also evident from the paper of Professor Lennard-Jones.

Dr. G. H. Dieke (*Groningen*), said : The diagrams which Professor Curtis * shows illustrate very well the anomalous behaviour of the helium bands. The figures give a good idea of the structure of the P- Q- and R-branches of the actual bands. In order to get a good picture of the theoretical significance of the anomalies another kind of diagram is often very convenient. It does not refer to the lines of the bands but directly to the rotational energy levels of the molecule.

The two figures will serve as examples. Fig. 1 is a theoretical diagram of a d-complex. (Value of the total quantum number n and the azimuthal quantum number l of the valence electron given ; all possible orientations with respect to the internuclear or the rotational axis.) The structure of such a complex depends entirely on the strength with which the orbital moment of momentum of the valence electron is coupled to the internuclear axis, and the strength of coupling can be expressed by the coupling constant α which is 10 in our particular case. If α should be very large, we should have Hund's case (a), and the energy of the molecule would to a first approximation be given by $const + Bj(j + 1)$. As we are only interested in the deviations from this case, we subtract $Bj(j + 1)$—which is common to all terms—from the energy

[4] *Arkiv Mat. Ast. Fys.*, **20A.**, 1928. [5] *Roy. Soc. Proc.*, **A122**, 219, 1929.

* See page 699.

values which the theory of band complexes allows us to calculate. These reduced energy values are represented graphically as a function of j. (In the figure $B = 1$.) Such a j-diagram should show only horizontal lines if the coupling with the internuclear axis should be very large. The deviations from the horizontal lines represent the influence of the change of coupling on the rotational energy values. For large values of j the orbital momentum is quantised with respect to the rotational axis, and if ρ is the component of l along that axis the rotational energy is again a quadratic function of j, namely $B(j-\rho)(j-\rho+1)$.

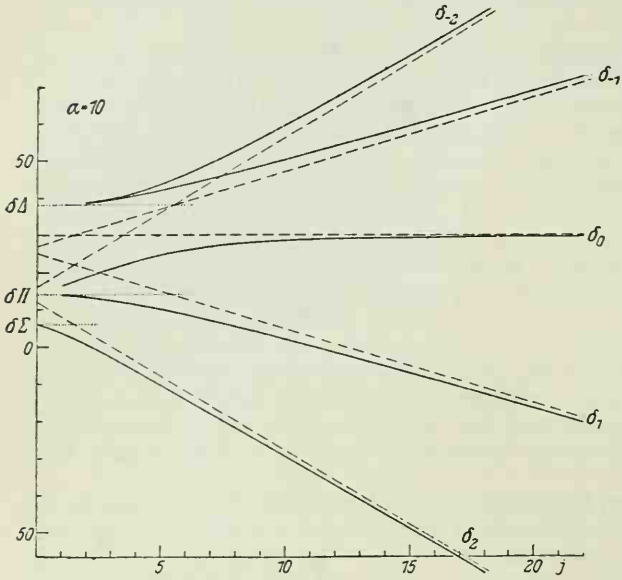

FIG. 1.—*Theoretical d-complex.* According to the new nomenclature the small Greek letters must be replaced by the corresponding Latin ones.

This can be seen in the diagram by the approach of the lines representing the energies to the five asymptotes.

Fig. 2 is a diagram of the empirical $4d$-complex of the He_2 triplet system which is the initial state of the strong bands of complicated structure near λ4400 ÅU. The relative energy values can be obtained by combination relations and a value of B can be calculated. $Bj(j+1)$ is subtracted from the energy values and these reduced energies are represented as functions of j, as was done in the theoretical diagram.

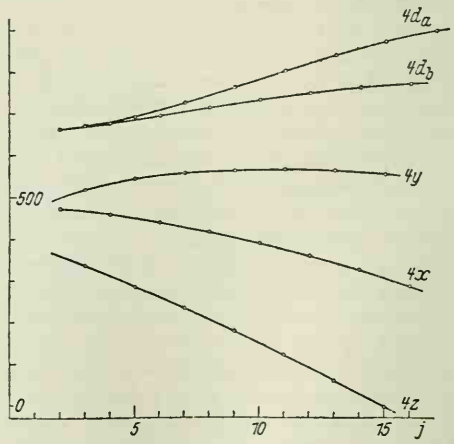

FIG. 2.—Diagram of the empirical $4d$-complex.

A comparison of the two figures shows immediately how the different energy levels of the empirical complex ought to be interpreted; for the similarity of the two figures is very striking. In the empirical diagram the curves tend to bend downward for large values of j. This is due to the distortion of the molecule by centrifugal forces which was not taken account of in

the theoretical treatment. The diagrams show that the theory is very well able to give account of the sometimes very complicated and anomalous structure of the helium bands.[6]

Professor Mecke (*Bonn*), said: Professor Henri's work on polyatomic molecules * is of particular interest. These molecules are of special interest to chemists, for most of them are stable and their chemical properties are well known. On the other hand most of the diatomic molecules are unsaturated compounds unknown to the chemist. Nevertheless, as intermediate compounds, they will be very useful in the investigation of the mechanism of a chemical reaction. Considering now the spectroscopical behaviour of the molecules, we can readily analyse the spectra of diatomic molecules and we can tell the chemist many things useful for his work, such as the size of the molecule, the vibration frequencies, the energy of dissociation, the different electronic states, etc., but we know practically nothing about the spectra of more complex molecules. It is now time that investigations were concentrated on these problems, and Professor Henri has already done much preliminary work of this kind.

I should like to ask Professor Henri a question concerning his investigations on NO_2. I tried to analyse the absorption-spectra of several simple polyatomic molecules, such as H_2O, NH_3 NO_2, etc. In my paper I say something about the spectra of ammonia and water-vapour; but I did not succeed in analysing the very complicated spectrum of nitrogen dioxide (NO_2) in the visible region of the spectrum. Now it appeared to me that the absorption-spectrum in the ultra-violet shown by Professor Henri is far more simple, and I would ask whether he has been able to analyse the bands of this spectrum so that he can determine the three moments of inertia and the shape of the molecule, including the vibration frequencies and, further, if he can show that these two absorption-spectra in the visible and in the ultra-violet have the same initial (lower) electronic state which they ought to have.

Dr. E. B. Ludlam (*Edinburgh*), asked: Could M. Victor Henri tell us what success he has had in regard to the *quantitative* effect of temperature in predissociation? Has pressure any effect? Is it quite certain that collisions do not play a part in producing the pre-dissociation?

Mr. C. P. Snow (*Cambridge*), said: The results of Professor Henri upon the increase in the number of predissociation bands by raising the temperature would appear to be explained by an extension of the theory of O. K. Rice.[7]

Professor H. Volkringer (*Paris*) said: It would be of interest to compare the modifications induced in absorption band spectra by increase of temperature with those observed in emission in the case of metallic vapours. I refer particularly to the emission spectra obtained by electrodeless discharge with zinc vapour. In this case, in fact, on increasing the temperature the bands with fine structure disappear and we obtain diffuse bands on a continuous background.

Dr. G. Herzberg (*Bristol*) said: (1) I wish to emphasise that only in some cases where the energy content of a molecule is higher than the dissociation energy of the normal state does predissociation occur. In fact, in diatomic molecules predissociation does not usually

[6] For further particulars I must refer to *Z. Physik*, **57**, 71.

* Page 765.

[7] *Physical Rev.*, **33**, 748; 1929, *cf.* Kronig, *Z. Physik*, **50**, 360, 1928, and Gibson and Rice, *Nature*, **123**, 347, 1929.

occur, as is well known, *e.g.*, in the case of N_2 and also in the case of some polyatomic molecules; for instance, the molecule CH_3I (according to the work of Professor Scheibe and myself) * has a continuous spectrum at about $\lambda 2500$ which obviously corresponds to a dissociation of the molecule and has a series of very sharp bands far in the ultra-violet at about $\lambda 2000 - 1600$. This means that the CH_3I molecule has a set of quite sharp discrete levels considerably higher than the dissociation energy of the normal state without any sign of predissociation.

(2) I should like to ask Professor Henri whether he has any detailed explanation of the temperature effect on the predissociation of molecules. It must be pointed out that it seems quite impossible to assume an influence of the temperature on the transition probability from the discrete into the dissociated state (predissociation), or an influence on the excited molecule by collison with other molecules, since the life time is too short. Therefore, I believe that the effect of temperature on the predissociation of molecules found by Professor Henri is due merely to the well-known alteration of distribution of molecules over the different rotational and vibrational states of the normal electronic state according to the Boltzmann factor $e^{-\frac{E}{kT}}$. For with increasing temperature the distribution curve for the rotational levels becomes broader and flatter and more vibrational levels are excited in the ground state so that the observed behaviour may result.

Professor Henri (*Zürich*) in reply said: The complete analysis of the absorption spectrum of NO_2, which is much simpler in the far ultra-violet, will be given in a paper to appear shortly.

The quantitative study of the influence of temperature on the limit of predissociation has given good results for the calculation of the molecular specific heats of several organic molecules. For example, for C_6H_6 we get by absorption spectrum C_v 28·5, and by calorimetric measurement 25.

The influence of pressure on the limit is very small; to produce an appreciable effect a pressure of about 10 atmos. is necessary, as shown in my laboratory by Teves.†

Professor Grimm (*Ludwigshafen*) said: In Professor Birge's paper ‡ 6 and 9·1 volts are mentioned as the most probable values for the heat of dissociation of oxygen and nitrogen. If again we take the heat of dissociation for 4 C—C linkages (which is approximately identical with the heat of sublimation of 2 moles of diamond) we have the following figures

	4(C — C)	N ≡ N	O = O
Heat of dissociation	12	9	6
	4·3	3·3	2·3

That is to say, it might be suggested that each non-polar linkage of one of the three neighbour elements C, N, O, requires approximately the same amount of energy for the dissociation. This is, perhaps, more than a mere matter of chance.

Dr. R. C. Johnson (*London*), said: The results which Professor Birge has given us will be of considerable value in providing more accurate data on Heats of Dissociation. These data are not only of interest for their own sake, but they are of very great importance in

* A preliminary report is found, p. 716.
† *Z. Physik*, 1927. ‡ See page 707.

the determination of the detailed electronic structures of molecules. It is, however, very remarkable—as Professor Birge has shown—that the $E_\omega : \omega$ curve is a synthesis of two parabolas, and it would seem evident that some change in molecular structure takes place at this point of the loading of the molecule with vibrational energy. The precise nature of this change is of considerable interest. We may look for the cause of the change in those phenomena which accompany the diminishing strength of the inter-nuclear electric field. We should in fact expect the molecule to pass successively through the conditions of cases (3), (2), and (1) to which I have made reference in my paper. A restoration of the l_τ couplings and the $l : s$ coupling should take place in each atom. It is difficult, nevertheless, to conceive of any discontinuity arising from this process. There is, however, one process in molecule formation which, by its very nature, must be discontinuous, *viz.*, the " promotion " of electrons, and it is suggested that the converse of this which may be styled " de-promotion " provides an explanation of the sudden change referred to above. This critical point will therefore mark the change from quasi-molecular to true atomic conditions (as prescribed by the Pauli principle) within the component atoms.

Dr. G. Herzberg (*Bristol*) said : Professor Birge concludes in his paper from the linearity of the $\omega_n : n$ curve for the normal level of N_2 that the extrapolated value of 11·7 volts for the dissociation energy has a real meaning and that, therefore, normal N_2 dissociates on increasing the vibrational energy into one normal ^4S atom and one excited atom in the ^2D state. I would like to emphasise, that according to the theoretical work of Wigner and Witmer, a $^1\Sigma$ state, which is the ground state of N_2, can never result from a ^4S and a ^2D state, as is easily seen by addition of the spin vectors. It is not to be expected that purely theoretical considerations would lead to a result which is so different from that obtained by successively increasing the vibrational energy. I, therefore, believe that the extrapolation is wrong and the higher vibrational levels follow a ω_n-curve which has a negative curvature. Also, in other cases, a discrepancy exists between linear extrapolation and true values of the dissociation energy as *e.g.*, in the case of CO.

Dr. G. Herzberg (*Bristol*) said : Messrs. Kondratjew and Leipunsky (see p. 736) seem to suppose that recombination of atoms in a two-body collision can only occur if one of the atoms is excited. New experimental data [8] show that some homopolar molecules, *e.g.* CN and N_2^+, dissociate from the ground level in one normal and one excited atom, whereas they dissociate into two normal atoms from an excited state of the molecule. This means that they can be dissociated into two normal atoms by light absorption or inversely that the *normal* atoms may recombine in a two-body collision with light emission.

Professor Kondratjew (*Leningrad*) in reply wrote : Considering the elementary processes which might take place in the hot halogen vapours we also had in mind the process $X + X = X_2 + h\nu$, or (as is more likely in our case) the process $X + X = X'_2 + h\nu$. In order to ascertain whether such a process really exists we measured by means of a thermopile the total amount of radiant energy emitted by the vapours (in this case ν corresponds to infra-red radiation). However, no appreciable radiation could be detected. Therefore we can state

[8] G. Herzberg, *Ann. Physique* (4), **86**, 189, 1928; *cf.* also W. Heitler and G. Herzberg, *Z. Physik*, **53**, 52, 1929.

that the processes mentioned, if they exist at all, are in no way more probable than the process $X + X' = X_2 + h\nu$.

Professor Victor Henri (*Zürich*), said: The isotope separation for the vibration bands of phosgene $COCl_2$ is more feeble than in the case of Cl_2. The theory of the band separation in the case of diatomic molecules cannot be applied directly to polyatomic molecules. In the case of $COCl_2$ we found, with Howell, that the separation is twice as feeble as for Cl_2 and, moreover, $\Delta\nu$ does not vary proportionally with the vibration quanta—which is analogous with the case found by Curtis and Patkowski for ICl. It seems that in the case of ClO_2 according to Goodeve, the separation is also weaker than in the case of Cl_2. It would appear that the theory of the isotope effect for polyatomic molecules ought to be different from that for diatomic molecules.

Professor W. E. Curtis (*Newcastle*), said: I should like to suggest a possible explanation of some of the peculiarities noted in the absorption spectrum of ClO_2. On page 749 it is stated that "the fact that the origin of the isotope effect is not the origin of the system is still without explanation, as are also the sub-heads which have a positive separation. These latter only occur with the lowest frequency bands." It will be seen from the paper (p. 725) by Professor Patkowski and myself that both these features may be explained on the supposition that the progressions concerned do not originate in the lowest vibrational state of the molecule, but in some higher ones. Our Fig. 2 shows that only for Progression I is the isotope separation zero at the origin of the system; further, it should be reversed in sign for the lowest frequency bands of the higher progressions. It is also evident that for the latter the slope of the curve in the neighbourhood of the axis is necessarily less than that derived from the first progression, and this might account for the low value of the observed isotopic coefficient (see eqn. 6), although the calculated coefficient is, in the case of a polyatomic molecule, so entirely dependent on the model adopted that its value must be regarded as quite uncertain. This suggestion, of course, implies that the first progression at least is replaced by continuous absorption, and I should like to know what evidence the authors have in this connection.

May I also direct attention to the reversal in the paper of Goodeve and Stein of the usual practice of band spectroscopists of denoting the upper electronic level by ′ and the lower by ″. This convention is now too well established to be reversed without some risk of confusion arising. For similar reasons the "series" of this paper should be termed "progressions," and the so-called "sequences" given some more non-committal name, such as "groups" pending further evidence as to their true nature.

Mr. C. F. Goodeve (*London*) said: The suggestion of Professor Curtis is an important one, but I believe that the evidence from the isotope separation, particularly in a triatomic molecule such as ClO_2, does not outweigh the energy and intensity considerations on which the present arrangement is based. No evidence of the existence of lower progressions than those recorded was observed, which gives a further justification for the arrangement.

The authors agree with Professor Curtis that it is most desirable to standardise the nomenclature of band spectra. The origin of that used in the present paper has been indicated in footnote 4 on page 744.

PART II.—THE RAMAN EFFECT.

INVESTIGATION OF MOLECULAR STRUCTURE BY LIGHT SCATTERING.

By Professor Sir C. V. Raman.

Received 9th September, 1929.

PART I.

1. Introduction and Historical.

In the scheme of discussion organised by the Faraday Society, the phenomenon of the scattering of light of altered wave-length rightly occupies a position intermediate between the molecular spectra in the ultra-violet and the infra-red regions because it stands in intimate relation to both these fields of research. Before dealing with these relationships and indicating the kind of information it gives regarding molecular structure, it would seem proper to give a brief historical introduction to the subject.

Eight years ago we commenced at Calcutta an extensive programme of research on the phenomena of scattering of light in gaseous, fluid and solid media. The inspiration for this scheme of research was derived in the first instance from Rayleigh's well-known theory of the blue sky, and the hope that our laboratory studies would furnish a solid experimental basis for the explanation of such natural phenomena as the colour of the sea and the colour of ice in glaciers. It soon became clear, however, from our experimental results, that the work taken up by us would go far beyond this restricted purpose, and lead us to most valuable information on such fundamental problems as the constitution of the solid and liquid states, the structure and optical properties of molecules and the nature of radiation itself. In a little essay published by the Calcutta University in February, 1922, a preliminary survey was made of the whole field. In the concluding chapter of this essay, entitled "The Scattering of Light and the Quantum Theory," it was pointed out that if the process of scattering could be regarded as a collision between a light quantum localised in space and an individual molecule, the observed laws of light-scattering would be quite different from that anticipated on the classical principles of the electro-magnetic theory of light. According to the latter, the variations in the spacing and orientation of the molecules in the fluid and the consequent local fluctuations of optical density would determine the magnitude and characteristics of scattering, while according to the extreme light-quantum point of view, the individual scattering processes would be wholly incoherent with each other, and the resulting intensity of scattering would depend on the

density of the fluid as a whole, and not on its local fluctuations. Our experimental investigations in 1922 and 1923 showed that the theory of light-scattering based on the Maxwellian principles and the statistical thermodynamic concept of fluctuations were in substantial agreement with the observations. From the very first, however, evidence was encountered of the presence of a *disturbing effect.* In several *carefully purified* liquids, notably water, ether, the alcohols, and also in ice, optical glass, etc., it was unmistakably evident that the scattering of light contemplated according to the classical theories was accompanied by a radiation of altered wave-length. These observations were duly published at the time, and it may be therefore justly claimed that the existence of this new optical phenomenon had been established about the same time, and independently of the well-known work of Compton in the X-ray region. It will be recalled that Compton was inclined to attribute the softening of X-rays by scattering to what he called " a general fluorescent radiation " until his spectroscopic investigations gave an entirely different version of the matter. It is not surprising, therefore, that the optical effect brought into evidence by the Calcutta investigations was also labelled as a " *special type of feeble fluorescence.*" The difficulty of explaining its excitation by incident light of frequency far removed, both from the infra-red and the ultra-violet characteristic frequencies of the molecules, was obvious to me from the first. For this reason the further investigation of this phenomenon was definitely placed on the programme of research at Calcutta. Some attempts were made in 1924 and 1925 to make a spectroscopic study of the effect. Unfortunately, however, owing to the feebleness of the radiation, our attempts to photograph its spectrum were made using sunlight, with coloured glass filters as the exciting radiation, and the results obtained did not prove sufficiently encouraging.

2. The Nature of the Effect.

The true nature of the phenomenon became evident to me for the first time towards the end of 1927 when engaged in an attempt to explain the Compton-Effect as due to a kind of fluctuation in the state of the scattering atom in the field of radiation. The ejection of the electron from an atom is obviously a very violent kind of fluctuation in its electrical state. Much milder types of fluctuations are obviously possible, and would give rise to a change of wave-length in light-scattering by molecules according to the scheme,

$$\underset{\text{(normal)}}{\text{Molecule}} + \text{Radiation} \rightleftharpoons \underset{\text{(excited)}}{\text{Molecule}} + \underset{\text{(degraded frequency)}}{\text{Radiation.}}$$

This idea was vigorously followed up, and the importance of using monochromatic light as the exciting radiation soon became evident. Connected accounts of the discovery and of its history were given in a lecture delivered to the South-Indian Association at Bangalore, on the 16th March, 1928, and published in the *Indian Journal of Physics*, on the 31st March, 1928. All the essential features of the phenomenon were set out in this lecture, namely :—

(*a*) Its universality, as supported by observations of it in gases, vapours, liquids, crystals and amorphous solids, also in a great variety of chemical substances, both organic and inorganic.

(*b*) Its spectral character, consisting of lines in some cases, more or less diffuse bands in others, and in addition, a more or less diffuse continuous spectrum accompanying the lines or bands.

(*c*) The theoretical explanation of the phenomenon, as involving an exchange of energy between the quantum and the molecule, and the equality of the change of frequency (positive or negative) to a characteristic frequency of the molecule, and the consequent utility of the phenomenon as an aid to the exploration of molecular spectra—especially in the infra-red.

(*d*) The possibility of an enhancement in the frequency in addition to the degradation of it, but the greater probability of the latter.

(*e*) The *strong* polarisation of the radiations scattered with altered wave-length.

(*f*) The distinctness of the new phenomenon from fluorescence, though in obvious relationship with it.

(*g*) Its analogy to the Compton-Effect, and the indicated existence of an X-ray scattering with altered wave-length of a more general type than the Compton-Effect.

(*h*) The incoherent nature of the radiation.

Since the publication of the paper, the subject has been extensively studied in other countries, and admirable contributions have been made to the subject, notably by Wood, Pringsheim, McLennan, Rasetti, Cabannes, Daure and others. A bibliography of the subject with 160 references and abstracts has been compiled by Dr. Ganesan, and has just been published in the *Indian Journal of Physics*.

3. Gases.

In the case of gases the intensity of the scattered light is very weak, but by the use of very high pressures, spectrographs of great light-gathering power, and intense intrinsic illumination, the difficulties of investigation may be successfully overcome. The great importance of working with gases is obviously that here the molecular freedom, both for rotation and vibration, is greatest, and hence the possibility arises of getting sharper lines and greater resolution than in the liquid state. The rotational frequencies in liquids manifest themselves as a diffuse spectrum or wings accompanying the principal lines. In gases and especially with light molecules, the rotational effects can be clearly resolved. Notable success in this direction has been achieved by McLennan, Wood and Rasetti. The importance of this development cannot be over-estimated as the moments of inertia of the molecule, and the coupling of rotation with vibration, are capable of determination from the measurements. So far, detailed reports have been made on HCl, NH_3, H_2, O_2, and N_2. Even in the case of large molecules, by using spectrographs of sufficient resolving power, important progress in this direction remains to be achieved.

4. Liquids.

Liquids are by far the most convenient to study the effect with, and a fair number, especially organic chemicals, have been examined so far. Amongst the investigators who have drawn important conclusions concerning the relation between chemical structure and the molecular frequencies, as determined by the method of light-scattering, I would

mention Daure in France, Kohlrausch and Dadieu at Graz, Petrikaln in Riga, Venkateswaran and Ganesan at Calcutta. Reference will be made later to this question, but I would like here to emphasise the great importance of a critical comparison of the data obtained in the liquid and the corresponding vapours. Ramdas' early work on ether vapour appeared to suggest the identity of the frequencies of the molecular vibration in the two states. It must be remembered, however, in the case of polar molecules, we have reason to believe that association occurs in the liquid state, and hence we cannot assume without critical examination that a vapour and a liquid would give identical frequencies. Indeed, some discrepancies have been noted already in NH_3 and HCl. Water presents a very notable example of molecular association. The structure of the band obtained with water and the change that occurs with rise of temperature has been studied by several investigators. The most detailed investigation appears to be that of Venkateswaran and Ganesan at Calcutta. These authors have also attempted to correlate the effects observed with water and with ice. It would be of interest to investigate water-vapour and connect the three together by quantitative study. The field for the study of the effect in liquids offered by organic chemistry is so vast that only a small fraction of the substances offering themselves have been studied as yet.

5. Mixtures and Solutions.

The important physico-chemical problem of the nature of solutions naturally offers itself for investigation by the method of light-scattering, and several investigators have already commenced work on the subject. The most promising question is that of the completeness (or otherwise ?) of dissociation of electrolytes in solution. The subject has received attention from Carelli, Pringsheim and Rosen, Daure, Venkateswaran and Ganesan, and others. Perhaps the most interesting results are those of Daure, who examined a number of chlorides. He found that CCl_4, PCl_3, etc., give sharp lines corresponding to the M—Cl bond. The results obtained with bismuth and antimony chlorides in solution showed a broadening of the lines with increased dilution until they finally disappeared. Ganesan and Venkateswaran similarly find that the well-known bands due to water in aqueous solutions of H_2SO_4, HCl, HNO_3 acids, become sharper and sharper with increasing concentration of acid. These results appear very significant.

The similarities exhibited by solutions of carbonates of different radicals and similarly of the sulphates and nitrates amongst each other appear to support the idea that the characteristic frequencies are those of the ionised acid radical. Much, however, remains to be done in this field of research, particularly in the direction of the exact quantitative study of the mixtures of liquids, the constituent molecules of which are believed to associate or combine with each other.

6. Crystals and Amorphous Solids.

As already mentioned, ice was the first crystal in which the spectral character of the scattered radiation was examined and reported. It has a special interest, as it is perhaps the only substance in which direct comparison of the solid and the liquid state has been published so far. Subsequently, observations of the effect in various other crystals have been reported upon, notably quartz, calcite, gypsum, topaz, and Rochelle salt.

The case of gypsum, which has been examined by K. S. Krishnan, is perhaps the most interesting of all. As is well known, this substance contains two molecules of water of crystallisation. Krishnan found, from photographs taken with large dispersion, that in addition to the wave-lengths which could reasonably be attributed to the SO_4 radical, three sharp lines, at 2·8, 2·9, 3·0μ respectively, were obtained. These evidently are due to the water of crystallisation, and it is worthy of note that they are practically in the same position as the components of the band observed with water and ice though considerably sharper than even in the case of ice. The relative intensities in the three substances are, however, different. The comparison with the data for strong H_2SO_4 solutions given by Ganesan and Venkateswaran is also of interest. It would seem that even in concentrated acid solutions, an approach is made towards the state of H_2O in the solid crystal.

Another point of great interest is as regards the degree of sharpness of the lines obtained with the crystals. In the photographs taken with calcite and quartz by Krishnan in July, 1928, this is the most striking feature. With rise of temperature, however, the lines become diffuse, and in amorphous quartz becomes so diffuse that Pringsheim failed to observe them. Recently, however, Gross and Romonova have succeeded in photographing the diffuse bands with fused quartz and optical glass. The latter had been previously observed visually at Calcutta in the very first studies. Langer reports having obtained very diffuse lines with Rochelle salt. All these facts of observation may, perhaps, be connected by the general idea which I entertained from the first that the more perfect and ordered the arrangement of the molecules in a space lattice, the sharper would be the lines in the scattered-spectrum. It is well known from X-ray work that only relatively few crystals really give perfect X-ray reflections, and that in order to account for the facts, a mosaic theory of crystal structure is now generally believed in. The theory of imperfection of crystals developed by Smekal, Zwicky, and others may be recalled in this connection. It would seem that the scattered light furnishes with a measure of the perfection or otherwise of crystals, just as X-ray diffraction does. This idea, however, requires further investigations for complete establishment. The failure to obtain the evidence of the effect in rock salt, sylvine, etc., has been explained as due to the ionic nature of the lattice of the crystals. How far the well-known imperfections of the rock-salt as a crystal contributes to failure is a matter for consideration. It is not unlikely that many crystals will offer themselves for investigation for light scattering. The difficulty of course is to grow a sufficiently large and clear crystal.

7. Intensity and Polarisation.

It cannot be over-emphasised that measurements of the frequencies of the radiations appearing in light scattering do not, by themselves, give the maximum of information available by such studies. It is necessary also to obtain quantitative information regarding the intensity of the new lines, both relatively to the lines of unaltered wave-length and to the incident radiation. Further, the state of polarisation of the lines is also a matter of great importance. In the first report, and also more fully in the papers contributed in collaboration with K. S. Krishnan, the principal features were clearly emphasized. In the first place, the intensity of the new lines (absolutely) increases rapidly with the decreasing

wave-length of the incident radiations. This increase is analogous to the well-known Rayleigh fourth-power law of the classical scattering, and appears in some cases at any rate to be more pronounced. The different lines appear to be polarised to very different extents. Further, some of the lines corresponding to well-known infra-red absorption frequencies fail to appear in the scattered light. The absolute intensity of the scattered radiation with altered wave-length is much smaller than of the classical scattering.

While these qualitative results are of general application, obviously much more precise statements are essential, and it is here that there is the greatest scope for future research. The subject has received attention also from Pringsheim, Cabannes and Daure and others. As yet, however, the information available is very meagre.

The fact that the different lines are differently polarised is obviously fundamental. The question of intensity is essentially related to that of polarisation. If we understand completely why some lines are strongly polarised and why others are weakly polarised, we would at the same time get a clear comprehension of why some infra-red absorption lines fail to appear in scattering and *vice versa*. Incidentally, it may be remarked that the lines corresponding to vibration frequencies of the molecule would stand on a different footing from rotation lines, or from rotation-vibration combination lines. Each of these classes would have to be separately studied. Then, again, the question arises, how the intensity and polarisation would be influenced by change of state. The work of Ramdas seems to suggest that probably we have merely an enhancement of the intensity in proportion to density, without a change of polarisation in the new lines. This, however, is far from being established, and it may even prove to be untenable. The impedance to free rotation in the liquid state must profoundly influence the rotational transitions, and hence also the intensity of the scattered radiation in general. In this connection work with liquids at low temperatures or under high pressures would be of value. It is not unlikely that a broadening of the lines and a development of a continuous spectrum may be noticed. An effect of this kind has, indeed, already been observed by Venkateswaran in glycerine, even after careful purification.

It may be pointed out that even as regards the polarisation of light scattered without change of wave-length, the information available is not adequate. Some recent work by P. V. Krishnamoorthy at Calcutta seems to indicate that in liquids at any rate, the depolarisation of the classically scattered light shows a very rapid increase as we approach towards the ultra-violet. The theory of anomalous dispersion, indeed, leads us to anticipate the existence of some such effect. Further investigations on this topic, however, would seem very desirable. Mr. Krishnamoorthy has also found that the ratio of intensity of the new lines to the old lines is considerably larger than was previously supposed. Daure has also reported results supporting Krishnamoorthy's work. It may be remarked here that in liquids the ratio would be considerably larger than in vapours. This is a consequence of the thermodynamic theory of the classical scattering.

8. Relationship with Ultra-Violet and Infra-Red Spectra.

It is obvious that having ascertained the characteristic molecular frequencies—rotational, vibrational, rotional—vibrational, and also elec-

tronic transitions, if any, we can proceed to utilise the data for an interpretation of the molecular spectra of the ultra-violet, and also for understanding infra-red absorption and emission data. The question of possible alternative formulations of the fundamental energy levels of the molecule will naturally arise here. The evidence, however, seems fairly clear that the vibrational frequencies observed in light scattering are really fundamental frequencies, and *not* due to inter-combination between the fundamental vibrational frequencies of the molecule. This would seem to be fairly clear from the comparative data for substances with similar chemical constitution, but with atoms of differing weight in the molecule. Daure's results with a series of chlorides and Ganesan and Venkateswaran's results on bromoform, as compared with chloroform, show a remarkable and parallel shifting of the frequencies observed in light scattering towards longer wave-lengths with increasing weight of the substituent atoms. It would be incredible that such beautiful parallelism would be observed if the frequencies were differences of the fundamental frequencies of the molecules, and not the latter themselves.

Several papers have already appeared on the interpretation of ultra-violet absorption and fluorescent spectra, and of the infra-red absorption spectra with the aid of the results from light scattering. Obviously, however, an immense amount of work remains to be accomplished.

The data already obtained with organic liquids show how, in quite a number of cases, it is possible to identify particular frequencies with vibration of particular chemical bonds in the molecule. Apart from the frequencies as measured, it is fairly certain that a study of the polarisation character of the new lines would enable a further advance to be made in this direction. It is found, for instance, that the frequency corresponding to the C—H bond in aliphatics and aromatics is different, and that the polarisation is even more strikingly so.

9. Theory of the Effect and its Relation to Molecular Structure.

The theory of dispersion in the form which it takes on the wave-mechanics formally explains the phenomena of light scattering. Several attempts to formulate the theory in a more concrete form so as to fit in with facts observed in particular cases have already been made. Special reference may be made here to Professor Kemble's explanation of Wood's observations with hydrochloric acid gas. The Dirac theory has also been used by two Italian writers, Amaldi and Segre, to give a general interpretation of light scattering and its relation to fluorescence. In a separate communication, I shall endeavour to indicate what would seem to me to be a promising line of further attack on the whole question of the relationship between molecular scattering of light, infra-red absorption, and the theory of dispersion.

PART II.*

Faraday was not only the greatest experimental physicist of the nineteenth century, but by his discovery of benzene can claim to be regarded as one of the founders of modern chemistry. It is therefore

* Substance of an oral address given at the Bristol meeting by way of supplementing the written paper bearing the same title (see Part I. above) which was printed and circulated in advance. Part I. was mainly historical in character.

very appropriate that the Faraday Society should offer itself as a forum for the discussion of a new phenomenon which forms a kind of bridge between the sciences of physics and chemistry. As explained in my written paper, its discovery was no accident, but was the result of systematic research on the subject of the molecular scattering of light continued for several years in the hope that results of a fundamental character would be reached. It is proposed in this address to deal with the explanation of the phenomenon and with its relation to molecular structure, problems of deep interest to physicist and chemist alike.

In the first day's discussion we heard a good deal about spectroscopic nomenclature and especially about the very large number of symbols necessary to describe the physical state of a molecule in its electronic, vibrational, and rotational energy levels. It may not, therefore, be superfluous to emphasise that a molecule, in spite of this apparent complexity of structure, is after all a single physical entity, and that its properties should be capable of being described in a simple manner. The study of the phenomena of light-scattering and also certain related investigations conducted at Calcutta on electric and magnetic birefringence of fluids disclose that many of the polyatomic molecules familiar to the chemist possess very remarkable properties. Chief amongst them is the possession, in many cases, of extraordinary degrees of optical, electrical and magnetic anisotropy.

As an instance of the new results reached at Calcutta in this direction we may refer to the cases of the aromatic hydrocarbons, benzene, naphthalene, and anthracene. The crystalline birefringence exhibited by the two latter substances has been recently measured by Mr. Bhagavantam and has been found to be about twice and thrice as great respectively as that of calcite. High as is the degree of optical anisotropy indicated by these measurements, even more remarkable is their magnetic anisotropy established by observations with the crystalline solids. The naphthalene and anthracene molecules have a diamagnetic susceptibility about four and five times respectively greater in a direction normal to the plane of the carbon rings than the minimum value in a direction parallel to the plane. The aromatic and aliphatic series of compounds of carbon offer a most interesting contrast in this respect. As was found several years ago by Cotton and Mouton, benzene and the aromatic compounds of carbon generally in the fluid state show strong magnetic birefringence similar to that of a *positive* uniaxial crystal. By means of a specially constructed electromagnet, we have been recently able to detect the magnetic birefringence of the aliphatic hydrocarbons, and Mr. Ramanatham's measurements with them show the birefringence to be very feeble and similar to that of a *negative* uniaxial crystal. These observations indicate that the well-known chemical differences between the aromatic and aliphatics correspond to a difference in their magnetic characters which is so striking and significant that it may not be too much to say that the ultimate explanation of the facts of organic chemistry may be found *via* the studies of magnetic behaviour of carbon compounds.

In the case of the benzene molecule, our studies of light-scattering and of magnetic birefringence enable us definitely to assert that a direction normal to the plane of the carbon atoms is an axis of *minimum* optical polarisability and of *maximum* diamagnetic susceptibility. On the other hand, we have convincing reasons for believing that in the triatomic molecules of CO_2 and CS_2, the line joining the centres of

the atoms coincides with the direction of the *maximum* optical as well as of the *maximum* diamagnetic susceptibility. The explanation of such facts concerning the optical and magnetic characters of different types of polyatomic molecules in terms of the electronic configurations in them offers itself as an important problem for the spectroscopists to solve.

It was in the attempt to investigate experimentally how the optical anisotropy of molecules varied with the wave-length of the incident radiation that we were led at Calcutta to the discovery of the existence of scattered radiations with altered wave-length. Before dealing with this phenomenon, we may venture to turn from the problems of spectroscopy to some physical considerations regarding the scattering of light by molecules.

Investigations on the molecular scattering of light of the classical kind show very clearly that the intensity of such secondary radiation stands in the closest quantitative relationship with the refractivity of the molecules. The classical theory of dispersion also teaches us that the refractivity of molecules for visible rays and for radiations in the near ultra-violet is determined by the existence of characteristic molecular frequencies lying mainly in the far ultra-violet region of the spectrum.

When light is scattered by a molecule, the incident radiation has usually a frequency less than the characteristic ultra-violet frequencies of the molecules ; hence the energy of the incident quantum of radiation is insufficient to cause the electrons in the molecule to pass definitely into a higher energy level. Nevertheless, it is the tendency of the incident radiations to disturb these electrons that is responsible for the classical scattering of light. As the characteristic *infra-red* molecular vibrations or rotations contribute to a negligible extent to the refractivity for visible light, it follows that they do not play any important part in the process of light-scattering as conceived in the classical theory.

We may, at this stage, ask ourselves, how are we to explain the fact that the classical type of scattering is actually accompanied by radiations of altered wave-length ? In my very first report, I suggested a simple and easily understood picture of the process involved in this new phenomenon. The quantum of radiation exchanges energy with the molecule on which it is incident. Part of the energy of the quantum is taken over by the molecule which thus passes into an excited condition. *Vice versa*, an excited molecule may give up its energy to the quantum which then goes off with increased energy. The first process naturally occurs more frequently, as there are more unexcited molecules than excited ones. The process pictured is one which can actually occur, for the incident quantum of energy is greater than the quantum of energy absorbed by the molecule ; that the interpretation is a valid one is shown by the fact that the difference between the frequencies of the incident and scattered radiations is characteristic for the molecule, and in not a few cases agrees with known infra-red absorption frequencies.

Several writers have criticised this simple picture of the process of light scattering as inadequate. I believe these criticisms are based on a misapprehension. It is true that the theory of dispersion in the form which it takes in the quantum theory involves the consideration of three different levels of energy A, B, and C of the scattering system, and that the change of frequency which occurs in the scattering process is the difference between the energy quanta required from a transition

from A to C, and from B to C. The ultimate result is, of course, a transition of the system from A to B. The critics have, it seems to me, overlooked the fact that in the cases with which we are actually concerned, the introduction of the third level C is merely a mathematical device. The fact that the scattering with altered wave-length is usually only a feeble addition to the classical type of scattering, and that its intensity increases rapidly with increasing frequency of the incident radiation, indicates that the third level C with which we are chiefly concerned is an electronic level corresponding to a characteristic frequency of the molecule in the far ultra-violet. When the incident light is in the visible or near ultra-violet, its quantum of energy is insufficient actually to cause the molecule to pass over into the state C, and the transition of the molecule assumed for the purpose of the calculation is a purely virtual one which cannot actually occur. There is an interchange of energy between the molecule and the quantum only if the initial and final states of the former are different, and the frequency of the scattered radiation depends only on the difference of these two states.

We may at this stage, endeavour to picture to ourself in greater detail the process which causes the molecule to go over into a different state of energy as the result of the radiation falling upon it. There are two types of physical theory which experience proves to be useful in the exploration of a new field of research. The first is the *a priori* or fundamental type of theory based upon a deep analysis of all the elements involved in the problem. The second is the phenomenological theory which accepts the observed facts and endeavours to connect them with other observed facts in a coherent manner. The former type of theory is the more ambitious, and we may venture to hope that some day it will be possible to work it out in full detail, for our phenomenon. Meanwhile, however, and especially in the case of the polyatomic molecules so important to the chemists generally, it seems probable that progress will be achieved more quickly with the aid of theories of the phenomenological type.

In the first place we may ask ourselves, why does the impact of radiation cause the molecule to change its energy-level of vibration or rotation? The answer to this is, very probably, that while the effect of the light on the molecule is primarily to disturb the electrons in it, there must be a tendency to alter at the same time also the rotational and vibrational energy-levels. The spectroscopist knows very well that it is only an approximation to regard changes in electronic, vibrational and rotational energy-levels of a molecule as independent of each other. In reality, all three are connected with each other, and it is impossible for the incident light to disturb the electrons in the molecule without at the same time tending to disturb the atomic nuclei and also the molecule as a whole and thereby altering its state of vibration and spin. If the classical notions of mechanics were valid, all three types of disturbance would occur simultaneously. In the newer physics, we should say that the probabilities of the three types of transition occurring in any given molecule are definitely related to each other. If the interconnections of the three types of transition are known empirically from the spectroscopic data for any given molecule, we could proceed from them to calculate the behaviour of the molecule in light-scattering, or *vice versa*.

The case of radiation inducing a change in the spin-energy of the

molecule is the one in which it seems most hopeful to obtain a quantitative picture of the phenomenon. It would be quite inappropriate to regard this as a simple case of mechanical collision between two particles resulting in a spin being set up in one of them. What is actually involved is the mechanical action of the field of the light-wave on the electric charges contained in the molecule. If we assume that the molecule has no permanent electric moment, or decide to ignore the latter if it be present, the mechanical action on the molecule would be due to the reaction of the field with the oscillating electric doublet induced by it in the molecule. The resulting couple would vanish completely if the molecule were optically isotropic, as the direction of the field and of the doublet would then be coincident. Actually, however, it is known that all molecules are optically anisotropic, some molecules such as benzene, CO_2, CS_2, etc., strongly so. Hence such optical anistropy of the molecule makes it possible for the field of the light-wave to exert a couple on the molecule and alter its state of spin. It is interesting to notice that the available experimental evidence indicates the intensity of the rotational effect to be much greater in the case of strongly anisotropic molecules such as those mentioned above, than for molecules which are known to be more nearly isotropic optically, *e.g.* CH_4, CCl_4, etc. It is believed that the considerations set out above, when more fully developed with the aid of the new mechanics will furnish a basis for quantitative comparison with experiment.

We may now pass on to consider changes in the vibrational state of the molecule induced by the incident radiation. From thermodynamical considerations it is evident that the great majority of the molecules in a substance would be in the zero vibrational state at ordinary temperatures, and hence it is clear, especially in view of what has been said above regarding the nature of the transitions induced by light, that they must correspond to the fundamental vibration frequencies of the molecules. [In exceptional cases, harmonics of such vibrations, and summations of two fundamental frequencies may occur with low intensities.] It appears desirable to emphasise this point particularly because the contrary opinion expressed by Langer in a note to *Nature* dealing with the case of CCl_4, appears to have gained currency in certain quarters and is quoted by Professor R. W. Wood with approval in his communication to the Faraday Society. The figures given by Langer in his note in *Nature* do not prove his contention, as the observed absorption frequencies of CCl_4 in the infra-red can be explained with equal numerical accuracy and physically in a much more acceptable way by taking the frequencies in the far infra-red observed in the light-scattering as the fundamentals, and the absorptions in the near infra-red as summationals derived from them. [Indeed this has been done recently by another American writer in a paper in the *Physical Review*.] The view that the vibration frequencies observed in light-scattering are really the fundamentals is supported by very cogent and convincing evidence. Particularly striking in this connection is the fact that the frequencies found move further and further into the region of the remote infra-red with increasing atomic weights, as we should expect them to do if they were fundamental frequencies. The diagram given by Professor Pringsheim in his recent article in the *Handbuch der Physik* (Band XXI., p. 612, Abb. 5) from the observations of Daure is specially instructive in this respect.

To enable us to understand why the light in disturbing the electrons also tends to set the atomic nuclei in vibration, it appears advantageous to adopt the method of representation used by Professor Franck in his well-known theory of photochemical dissociation of molecules, and by Professor Victor Henri in the beautiful discourse which we have listened to on the work of the Zürich school of physical chemists with polyatomic molecules. For simplicity, we may consider a diatomic molecule and draw a graph connecting the potential energy of the atoms as a function of their nuclear separation. The graph exhibits a minimum at a distance of separation of the atoms corresponding to their position of equilibrium. If now the molecule passes into an excited electronic state, we have to draw a new graph corresponding to such greater energy, and the distance of the nuclei at the lowest point of the new graph will be different from the first. In other words, if we excite the electrons, there is an inherent probability that we also alter the nuclear separation of the atoms in the molecule. In the experiments on light-scattering, the incident radiation quantum has insufficient energy to make the electron actually pass into an excited state. But the tendency to do so is there, and hence it is to be expected that in a certain proportion of the encounters with the radiation-quanta, the molecules will absorb energy and pass into a higher vibrational state.

If the form of the potential energy graphs were known, it should be possible to express this tendency in a quantitative form and thus to determine the intensity of the light scattered with changed wave-length.

In the case of polyatomic molecules, our one-dimensional picture may be, in general, too simple and may require elaboration into a three-dimensional scheme connecting the excitation of the electrons in different directions with the probabilities of excitation of different types of nuclear vibration. In this way, the remarkable variation in the polarisation of the scattered radiations of different wave-lengths may receive a satisfactory explanation.

METHODS OF EXCITATION OF RAMAN SPECTRA.

By Professor R. W. Wood, *Johns Hopkins University.*

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The results which I have obtained in a study of the Raman effect of solids, liquids, and gases (which has occupied most of my time during the past year), have been published already in the *Philosophical Magazine*, but a short resumé of the methods employed, some of them not yet published, may be of aid to those entering the field.

The method of excitation originally employed by Raman (condensation of the light of the lamp at the centre of a bulb filled with the liquid) was never used, since it is very wasteful of light, as I learned many years ago in the study of the fluorescence of iodine and other vapours.

In its place I have employed the method used in this earlier work, and in the study of the resonance spectra of mercury vapour, the excitation being effected by the direct radiation from a lamp placed almost in contact with a tube containing the liquid, the whole being more or

less completely surrounded by a cylindrical reflector. In this way the entire radiation of the lamp is employed, and it is, in addition, beaten back and forth through the liquid or gas by the reflecting walls of the enclosure. The heating of the liquid under this powerful radiation was prevented by a water-jacket, two different types of tubes being employed, in one of which running water from the tap flowed continuously along the outer wall of the tube, while in the other, convection of a comparatively small amount of water combined with air cooling accomplished the purpose. If absorption of some of the rays of the lamp was desired, the colouring material was dissolved in the water. In this case a cooling system employing a small volume of water must, of course, be used.

In the choice of radiations for the excitation of the spectra, there are a number of points which must be carefully considered.

Since the scattering increases very rapidly with decreasing wave-length (Rayleigh's law of inverse fourth power), it might appear at first sight as if a monochromatic radiation in the remote ultra-violet would yield spectra with the minimum time of exposure. Such a radiation is suitable, however, only in the case of substances which show no appreciable absorption, fluorescence, or chemical change under the excitation. If, for example, we try to employ Hg 2536 in the case of benzol, the radiation penetrates to a depth of only a fraction of a millimetre, while if we use radiations of somewhat longer wave-length, the rays penetrate the entire liquid mass, but the strong fluorescence completely masks the faint Raman lines.

The presence of a continuous background in the spectrum of the source is very undesirable, and it is quite marked in the case of the mercury arc, which appears to be the only source of light employed up to the present, with the exception of the helium tube, which I have found to be far better and have used in all of my more recent studies. It must be remembered that the scattered light of unmodified wave-length has an intensity of some four or five hundred times that of the light giving the Raman lines, and the continuous spectrum of the source, scattered by the liquid may often drown out completely the fainter Raman radiations. This is frequently the case with a quartz mercury arc operating at high temperature. The trouble may be in part obviated by running the lamp with less current, but the best plan is to employ between the lamp and the tube a filter which absorbs that portion of the spectrum in which the lines of modified wave-length appear.

As an illustration of a case of this kind we may take the case of the irradiation of benzol or similar organic liquid by the light of the mercury arc from which the lines 4046-4077 have been removed by a solution of potassium chromate. The excitation in this case is by the close group of three lines at 4358, and as the greater part of the Raman spectrum lies in the region between this group and the mercury line 4915 (a region free from mercury lines) there is a wide clear space for the projection of the Raman spectrum. We have forgotten, however, the faint continuous spectrum of the arc which is powerfully scattered by the liquid, and overlies the Raman spectrum. This can be eliminated by means of a filter absorbing the green region, placed between the tube and the lamp. We must choose a filter, however, which does not weaken 4358 to any considerable amount. Fluorescein, or preferably a not-too-strong solution of cobalt sulphocyanate may be used for this purpose, the latter solution being made by the addition of cobalt chloride to ammonium sulphocyanate.

There are a number of other points to be considered. We must make the background against which the light-scattering fluid is observed as black as possible, and we must avoid scattering by, or reflection from, the front window of the tube. In studying the scattering by HCl gas, I found it necessary to enclose the entire path from the front bulb to the spectroscope with black paper to prevent reflection of the diffused light in the room from the bulbous end of the tube, and the surfaces of the lens employed for projecting the image of the luminous HCl column on the slit.

Multiple diaphragms must be employed to prevent light, reflected from the walls of the tube, from reaching the front window. These devices are more fully described in my recent papers.

Many organic liquids, supposed to be chemically pure, show strong fluorescence unless freshly distilled. This is invariably true of liquids furnished in cork-stoppered bottles, for cork contains some soluble resin (?) which is fluorescent. In distilling them, care should be taken to avoid contact of the condensing vapour with cork or rubber. Any suspended solid matter in the liquid is very objectionable, as it scatters the continuous spectrum of the lamp.

The light of the mercury arc, even when filtered, is not at all satisfactory, for the best that can be accomplished is a multiple excitation by the three lines at 4358, or the two lines 4046-4077. The best results that I have obtained up to the present time, were by excitation by a helium tube 9 feet in length wound up in a close helix. This surrounded a tube of ultra-violet glass (which I made during the war for another purpose) transmitting the strong helium line 3888 and very little else. The tube containing the liquid under investigation lies within this tube, the spectroscope looking down its axis.

Raman spectra of a dozen or more organic liquids obtained by this method of excitation are reproduced in the *Philosophical Magazine*. They have the following advantages over spectra obtained by mercury excitation :—

(*a*) The Raman spectrum is unique, *i.e.*, it is excited by light of a single wave-length, and lies spread out with practically no contamination by other lines.

(*b*) The spectrum lies within a region for which the photographic plate shows fairly uniform sensitivity, while with mercury 4358 excitation the strongest Raman lines fall at the position of minimum sensitivity of an orthochromatic plate (about 5000), and are only barely recorded.

(*c*) The shorter wave-length of the exciting light is a favourable factor.

(*d*) No water cooling is required.

(*e*) There is practically no continuous background.

Apparatus is now being constructed in which a hot-cathode, low-voltage helium tube, as developed in the Research Laboratory of the General Electric Co. at Schenectady, is to be employed for the excitation.

Preliminary experiments were also commenced, in which a parallel beam of light obtained by a lens was sent down a long tube filled with liquid. Here the faintness of the illumination is, in part, compensated by the great depth of the liquid irradiated. Two methods of observation were tried. In one the further end of the tube was drawn out into a black cone, as described in former papers, the spectroscope looking down the tube in the direction of the light by means of an oblique mirror. This method suffers from the disadvantage that the full light of the beam

is thrown directly down the cone, and the background is not black enough. Another method is to polarise the light initially, and point the spectroscope against the light, *i e.*, up the tube instead of down, shielding the slit from the exciting beam by a suitably-oriented nicol. What appears to be a still better method, if sufficient illumination can be obtained, is to employ an " end-on " quartz mercury arc, separating out 4046 with a monochromator rendering the light parallel and then sending it down the long tube into the black cone. The background in this case is black except for wave-length 4046, and this light serves merely to intensify and broaden the line of unmodified wave-length. An experiment was also made with a short tube illuminated as in these experiments to see whether any of the Raman radiation was " coherent."

Though it seemed highly improbable than anything but a negative result would be obtained, the experiment appeared to be worth trying, and it may be worth recording as a possible technique to be employed in other cases. (I tried it once with mercury vapour resonance radiation, in a slightly different form.) Suppose we sent plane-waves of monochromatic light, collimated from a point source, down the tube of liquid closed by windows of plate glass, and focus them upon the slit of a spectrograph. They will be united by the spectrograph, and we shall have the spectrum line represented by an intensely black dot on the plate. Radiations of modified wave-length, originating within the liquid, will not be focussed in a point on the slit, and the lines due to them will be of full length. The presence of anything like a system of plane-waves of modified wave-lengths, built up within the medium by the exciting waves, would show itself as a trace of a " dot " at the middle of each spectrum line. The source of light in this experiment was a pin-hole placed over the slit of a monochromator and emitting 4046 mercury light. No trace of coherence was found.

The great advantage of the long tube and monochromator method is that a single line can be employed for the excitation and the shortest wave-length compatible with the absence of absorption and fluorescence can be employed. It is obvious that the method is suitable only for substances available in considerable quantity. For fluids, of which only a few centimetres are available, the helium excitation is probably the best. The best method of exciting the Raman spectra of gases is worthy of careful study.

I reported in *Nature* last February the single line (corresponding to the Q branch) of HCl, excited in a tube 6 feet in length, filled with the gas and mounted alongside of, and in contact with, a 4-foot Cooper-Hewitt mercury arc in glass, the whole surrounded by a cylindrical reflecting shell of aluminium. A full description of the apparatus will be found in the *Philosophical Magazine.*

In the following number of *Nature*, Rasetti published a note on the Raman lines of one or two less corrosive gases. He employs a short tube of quartz cemented to a long steel tube which serves as the black background, and illuminates with a short quartz arc placed close to the tube. He now works with gases at 15 Atmosphere which, combined with the advantage of working with short λ excitation (Hg 2536), reduces considerably the time of exposure.

My impression is that the total light poured into the tube is about the same in the two cases, as I considered the question of whether to use a short quartz arc or a long glass one before beginning the work. The quartz arc is about fifteen to twenty times as bright as a glass Cooper-

Hewitt of the same length, but by making the latter fifteen times as long as the former, we get the same illumination, and the glass lamp and long gas tube can be completely surrounded by the reflecting shell of aluminium. I decided on this account to use the glass lamp, especially as I was not quite sure what effect radiations of wave-length 1849 and 2536 would have on the gas.

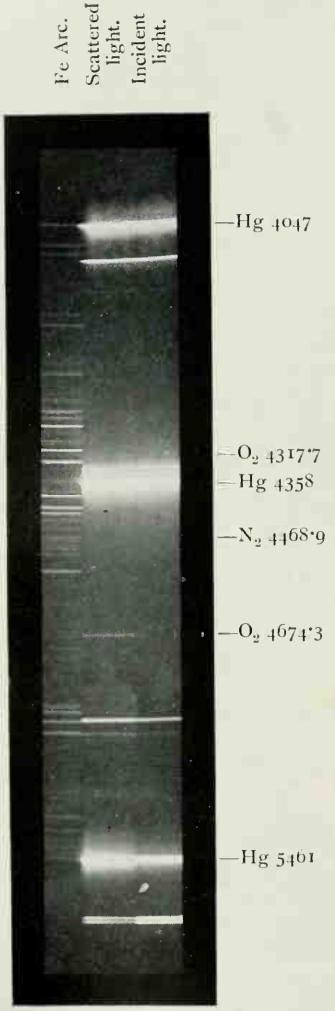
I propose to try next a quartz tube about 6 feet in length, surrounded by a glass tube, the space between filled with argon at low pressure containing mercury. Such a mixture, excited by moderate voltage, emits 2536 with great intensity relative to that of the other mercury lines. It might almost be described as a monochromatic lamp. The discharge is practically "cold," which is an advantage.

In my work on this subject, I have attempted to develop improved methods of excitation rather than study the spectra of a large number of substances. In the *Philosophical Magazine* a method is given by which the infra-red wave-lengths corresponding to the Raman lines can be read off at once from a scale mounted in register with a suitably-enlarged spectrogram. This obviates the necessity of making any wave-length measurements or calculations, but it can be employed to advantage only with monochromatic excitation. It holds, of course, only for the infra-red bands whose frequencies are the frequency differences between the exciting frequency and that of the Raman lines. Most of the lines in the immediate vicinity of the exciting line, which were formerly ascribed to absorption bands in the remote infra-red (30 to 90μ), are referable to known bands in the near infra-red, by the consideration of transitions between excited states of the molecule, as was shown by Langer, the hypothetical bands beyond 30μ indicated by Raman lines being mythical. Practically all of the organic compounds which I have examined show the Raman band corresponding to the infra-red absorption band at about 3·4μ. This Raman band has a very decided fine structure which varies from substance to substance, and a similar, though not identical, fine structure, has recently been found by one of our students in the absorption band at 3·4 of these same substances.

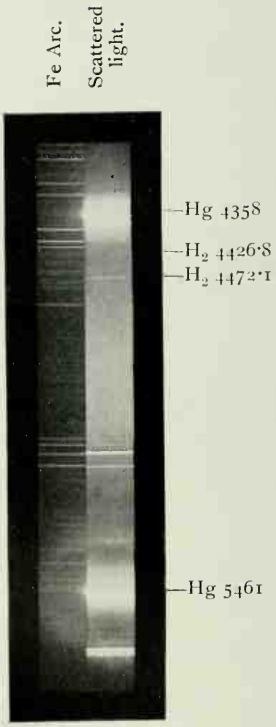
The resolution of the band into numerous finer components was accomplished with one of the new chromium-plated echelette gratings, which I have described recently in the *Philosophical Magazine*.

During the coming winter a more extended study of the relation of the band, as predicted from the Raman group of lines, and the group as observed in the absorption spectrum, will be carried on.

I am now having a spectrograph of higher dispersion constructed especially for the study of the Raman spectra excited by helium. In this connection it should be noted that a too dense flint glass cannot be used, as it refuses transmission in the neighbourhood of the 3888 helium line.



Raman scattering liquid air.
FIG. 2.



Raman scattering liquid hydrogen.
FIG. 3.

[*To face page* 797.

ON THE RAMAN EFFECT WITH LIQUID OXYGEN, NITROGEN AND HYDROGEN.

By Professor J. C. M. McLennan, F.R.S., *University of Toronto.*

Received 19th September, 1929.

Among the varied experiments carried out by numerous investigators on the Raman effect since its original discovery, those made by the writer in collaboration with his associate, Mr. H. J. McLeod, with liquid oxygen, nitrogen and hydrogen appear to merit special consideration. A preliminary account [1] of them has appeared elsewhere.

The apparatus used in these experiments is shown in Fig. 1. As the diagram indicates, the upper portion was provided with a Coil B, through which a gas to be liquefied such as argon could be led and the liquefication of this gas was provided for by the use of a suitable liquid refrigerant held in the specially-constructed thermos flask A surrounding the coil. The lower portion of the apparatus which was made wholly of glass, was the one used in making exposures for the Raman effect. It consisted of a four-walled, double thermos flask, about 25 centimetres long. When liquid air, liquid oxygen, or liquid nitrogen was under investigation, each was held in the inner thermos flask, while the outer one was kept filled with liquid air. When liquid hydrogen was under observation, the outer flask was kept filled with liquid hydrogen. The use of the outer liquid enabled one to keep the inner one free from visible ebullition, and subject only to very slow evaporation. For illumination 4 or 5 mercury vapour arc lamps were used. These were made of glass, and were about 30 cm. long. They were placed standing vertically close to, and surrounding the thermos flask containing the liquified gas. Each lamp carried a current of between 3 and 4 amperes. E and F were mirrors of platinum made by cathodic spluttering on glass. The light from the lamps entered the liquid laterally, and after being scattered, modified and reflected by the two mirrors, was focussed on the slit C of a high light-power spectrograph. Exposures of about 8 hours sufficed to record the Raman lines. Enlarged reproductions of spectrograms taken are shown in Figs. 2 and 3.

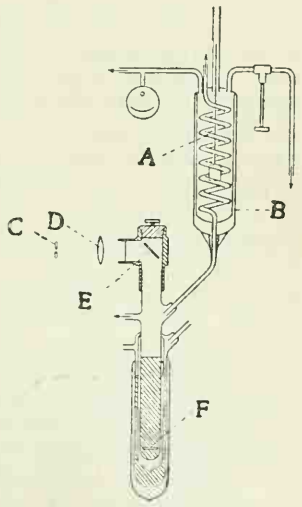


Fig. 1.

In our experiments with liquid air, we found that the spectrum of the light scattered included four sharp and clearly defined lines not included in the irradiating light, which was that from the mercury arc.

[1] *Nature*, Feb. 2, 1929; and *Trans. Roy. Soc. Canada*, Section III., 1929.

The wave-lengths of these lines were approximately 4317·7 Å., 4674·3 Å., 4468·9 Å., and 4849·3 Å. They, with their frequencies, are given below :—

Element.	Exciting Radiation.		Scattered (Raman) Radiation.			Observed.	Calculated from Band Spectra Data.
	(Å.)	(vac.)	(Å.)	Int.	(vac.)	cm.$^{-1}$.	cm.$^{-1}$.
Oxygen .	4046·6	24,705	4317·7	1	23,154	1552	1554
	4358·3	22,938	4674·3	2	21,387	1551	1554
Nitrogen .	4046·6	24,705	4468·9	1	22,371	2335	2331
	4358·3	22,938	4849·3	00	20,616	2322	2331

The experiment was repeated with pure liquid oxygen and again with pure liquid nitrogen, and it was found that the wave-lengths 4317·7 Å. and 4674·3 Å., only were obtained with liquid oxygen, and the wave-lengths 4468·9 Å. and 4849·3 Å., only with liquid nitrogen. The existence of two of the Raman lines with each liquid can be explained by supposing them to arise from irradiation by light of the two wave-lengths 4358 Å. and 4047 Å. The frequency difference for the mercury line 4047 Å. and the Raman oxygen line 4317·7 Å. is 1552 cm.$^{-1}$, and for the mercury line 4358 Å., and the Raman oxygen line 4674·3 Å. is 1551 cm.$^{-1}$. With the nitrogen lines, the one, 4468·9 Å., has a frequency difference with the mercury line 4047 Å. of 2335 cm.$^{-1}$, and the other, 4849·3 Å. with the mercury line 4358 Å.—a difference of 2322 cm.$^{-1}$.

It would seem that a mean vibration frequency of approximately 1551·5 cm.$^{-1}$ was involved in the Raman effect with liquid oxygen and a mean vibration frequency of approximately 2328·5 in the Raman effect with liquid nitrogen.

From the *Bulletin of the National Research Council*, Vol. II., Part III., No. 57, on " Molecular Spectra in Gases " (p. 232), 1554 cm.$^{-1}$ is indicated as the primary vibration frequency of the oxygen molecule in its normal state, and 2331 cm.$^{-1}$ as that of the nitrogen molecule in its normal state. Our results would suggest that the primary vibration frequencies were the ones involved in the production of the four Raman lines observed by us.

In experiments with liquid hydrogen irradiated with light from the mercury arc, we found that in addition to the usual mercury lines there were included in the spectrum of the scattered light lines correspondng to wave-lengths 4426·6 Å., 4473·1 Å., and 4863·5 Å. These, with their frequencies, are given below :—

Element.	Exciting Radiation.		Scattered (Raman) Radiation.			Observed.	Calculated from Band Spectra Data.
	(Å.)	(vac.)	(Å.)	Int.	(vac.)	cm.$^{-1}$.	cm.$^{-1}$.
Hydrogen .	4358·3	22,938	4426·6	2	22,584	354	347
	4358·3	22,938	4473·1	4	22,350	588	578
	4046·6	24,705	4863·5	1	20,556	4149	4159

By the use of suitable light screens, it was found that 4426·6 Å. and 4473·1 Å. were excited by the radiation 4358·3 Å., and 4863·5 Å. by radiation 4046·6 Å.

The frequency differences 354 cm.$^{-1}$ and 588 cm.$^{-1}$, it will be noted, are in the ratio 3 : 5.

In the original theory of the quantisation of the rotational energy of diatomic molecules, the energy of rotation is given by

$$E = \frac{m^2h^2}{8\pi^2I} = m^2h\,B \text{ where } B = \frac{h}{8\pi^2I},$$

m is the rotation quantum number, and I is the moment of inertia of the rotating molecule about the axis of rotation.

If we assume integral values for the quantum number $m = 0, 1, 2, 3,$ 4, etc., the rotational energy states will be given by

$$E = 0,\ Bh,\ 4Bh,\ 9Bh, \text{ etc.}$$

These, it will be seen, provide no transitions with $h\nu = E_1 - E_2$ that will give two rotational spectral frequencies in the ratio 3 : 5.

On the other hand, if we assume the half integral values $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$, etc. for m as Czerny [2] was led to do in explaining the rotation spectrum of HCl, the energy states will be given by

$$E = \frac{Bh}{4},\ \frac{9}{4}Bh,\ \frac{25}{4}Bh,\ \frac{49}{4}Bh, \text{ etc.}$$

If, now, we have a transition from the energy state $\frac{25}{4}Bh$ to the one $\frac{Bh}{4}$, and another from the energy state $\frac{49}{4}Bh$ to the one $\frac{9}{4}Bh$, we will have as a result two frequencies provided for having ratio 3 : 5.

This would, of course, afford an explanation of the frequency differences found in our Raman effects with liquid hydrogen, but it would involve the use of half-quantum numbers which is objectionable, and would besides require us to suppose that hydrogen molecules were continually in rotation when in their lowest energy state.

Wave mechanics, however, shows that the energy of rotation of a diatomic molecule is given by $E = Bhm(m + 1)$ with m having the integral values 0, 1, 2, 3, 4, etc.

This gives us energy levels

$$E = 0,\ 2Bh,\ 6Bh,\ 12Bh,\ 20Bh, \text{ etc.}$$

With these energy levels available, we see that a transition from $6Bh$ to 0, and another from $12Bh$ to $2Bh$ will provide us with frequencies in the ratio 3 : 5.

As we observed no trace of any Raman lines with liquid hydrogen with frequency differences in one or other of the ratios 2 : 3 ; 2 : 5 ; 3 : 4 ; 4 : 5 ; etc., it would appear that none such can exist.

We see, then, that in liquid hydrogen we have one set of molecules in which the transitions of rotation from $m = 2$ to $m = 0$ can occur, and a second set in which the rotational transitions $m = 3$ to $m = 1$ can occur.

[2] Czerny, *Z. Physik*, **34**, 227, 244, 1925.

Moreover, since 4159 cm.$^{-1}$ is known to be the frequency of the $m = 0$ to $m = 1$ *vibrational* transition for hydrogen molecules in the non-vibrational state, we have direct evidence that in liquid hydrogen (1) some molecules are in the zero vibrational and zero rotational states; and (2) others are in the zero vibrational and first quantum rotational states. As the intensity of the Raman line λ4473·1Å. was found by us to be between 2 and 3 times that of the Raman line λ4426·6, it follows that in liquid hydrogen one must have between 2 and 3 times as many molecules in the second, as compared with the number in the first state described above.

The distinctness of the two states is emphasised by the fact that no Raman effects were obtained corresponding to $m = 0$ to $m = 1$, or $m = 1$ to $m = 2$ rotational transitions.

The results of our experiments appear to be the first to constitute direct experimental proof of the correctness of Dennison's [3] view that hydrogen at low temperatures must be regarded as a mixture of two effectively distinct sets of molecules defined as symmetrical and anti-symmetrical by the theory of wave mechanics.

[3] Dennison, *Proc. Roy. Soc.*, **151A**, 483, 1927.

DEGRADATION OF LIGHT FREQUENCIES BY MOLECULAR SCATTERING.

By Professor J. Cabannes.

Received in French, 10th June, 1929, and translated by L. C. Nickolls.

1. The Wave Theory of Diffusion Spectra—Optical Pulsations.

A coherent theory of the molecular scattering of light is obtained by supposing that the light wave excites in each molecule an electric moment proportional to the field; these molecular doublets vibrate with the frequency of the exciting wave and radiate in their turn scattered waves. These small waves are completely extinguished by interference, except in the direction of regular propagation, provided the local irregularities caused by fluctuations of all kinds do not cause the production of a feeble residual light in all directions; this light is diffused light.

The authors of the theories of diffusion consider the molecules to be at rest in the medium. It is evident that, on this hypothesis, the frequency of the diffused light must be always equal to the frequency of the incident light.

The molecules, however, are not stationary; their relative positions, their orientation, their deformation, vary constantly owing to molecular motion. *There is no reason to suppose that the changes are infinitely slow; as a result the amplitude of the moment induced in the molecule by the incident light varies with time and the wave re-emitted by the molecule is not sinusoidal.* The molecular movements and the collisions must produce an increase in the diffused light, relative to the incident light; the rotation and vibration of the molecules must cause in the spectrum of

the diffused light, secondary lines on both sides of the principal line which is diffused without change of wave-length.[2]

If the spectrum of the incident light is composed of a single fine line, it should be found, that, in the spectrum of the emitted light, this line is broadened and accompanied by secondary lines.

Let us suppose that the incident line (frequency ω ; wave-length λ) travels along *ox* and the diffused light is observed along *oy* (Fig. 1) through a Nicol prism of which the principal section is supposed to be parallel to the plane defined by the two rectangular directions *oy* and *op*. The projection along the axis *op* of the electric moment induced in a molecule is written in the form

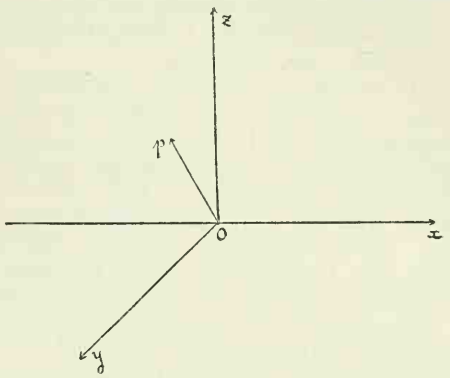


FIG. 1.

$$A_p = a_p \sin\left(\omega t - \frac{2\pi x}{\lambda}\right) \quad . \quad . \quad . \quad . \quad (1)$$

but a_p does not retain a constant value ; it is the sum of a fixed term and several varying terms ;

$$a_p = \bar{a}_p[1 + \epsilon_1 \cos(\alpha_1 t + \phi_1) + \epsilon_2 \cos(\alpha_2 t + \phi_2) \ . \ . \ .] \quad . \quad (2)$$

We have then

$$A_p = \bar{a}_p[1 + \Sigma\epsilon \cos(\alpha t + \phi)] \sin\left(\omega t - \frac{2\pi x}{\lambda}\right) \quad . \quad . \quad (3)$$

an expression which resolves into a sum of sines, each of which corresponds to a sinusoidal oscillation of the electric moment and to the diffusion of monochromatic radiation.

The frequencies of these diffuse radiations are : ω(the fundamental radiation, without change of wave-length) and $\omega \pm \alpha_1$, $\omega \pm \alpha_2$ . . . (secondary radiations). In the frequency scale, the diffusion spectrum is, then, symmetrical with respect to the fundamental radiation ; there are on one side the negative lines $\omega - \alpha$ of lower frequency and on the other the positive lines $\omega + \alpha$ with increased frequency.*

Maxwell's electromagnetic theory readily allows the calculation of the intensity of each of these sinusoidal moments, and the electric vector of the diffused wave (allowing for the retardation introduced by the propagation in the direction *oy*) is expressed as

$$\frac{4\pi^2}{\lambda^2 r}\bar{a}_p \sin\left(\omega t - \frac{2\pi(x+y)}{\lambda}\right)$$
$$+ \Sigma\frac{4\pi^2}{\lambda^2 r}\left(1 + \frac{\alpha}{\omega}\right)^2 \frac{\epsilon\bar{a}_p}{2} \sin\left[(\omega+\alpha)t - \frac{2\pi x}{\lambda} - \frac{2\pi y}{\lambda}\left(1 + \frac{\alpha}{\omega}\right) + \phi\right]$$
$$+ \Sigma\frac{4\pi^2}{\lambda^2 r}\left(1 - \frac{\alpha}{\omega}\right)^2 \frac{\epsilon\bar{a}_p}{2} \sin\left[(\omega-\alpha)t - \frac{2\pi x}{\lambda} - \frac{2\pi y}{\lambda}\left(1 - \frac{\alpha}{\omega}\right) + \phi\right] \quad (4)$$

[1] J. Cabannes, *La diffusion moléculaire de la lumière*, Paris (1929), édité par les Presses Universitaires de France.

[2] J. Cabannes and Y. Rocard, *J. Physique*, **10**, 52-71 (1929).

* Certain writers, on the contrary, describe as positive lines those with diminished frequency (but with longer wave-length). As the frequency occurs more directly in the problem than the wave-length, we think it better to apply the expression " Positive Lines " to those with increased frequency. They are also sometimes called " Anti-Stokes Lines."

In this expression, r signifies the distance from the diffusing medium to the observer; λ the wave-length of the fundamental radiation. The Σ's are extended to all the sine waves into which the variation of the amplitude a_p can be resolved.

The appearance of each pair of secondary lines can be considered as a result of the reaction between the incident wave ω and the oscillation α natural to the molecules.

It remains to determine exactly the origin of those natural oscillations. In perfect gases we have, principally, rotation of the molecules and vibration of their atoms. The frequency of these movements is given by the infra-red absorption spectra; the frequencies of molecular rotations are from 10^{12} to 10^{13}; those of atomic vibrations are about 10^{14}. The rotations, then, will give on each side of the fundamental line, *slightly dispersed secondary lines* (placed several Ångström units from the fundamental) while the intra-molecular vibrations will give *dispersed radiation* (several hundred units from the fundamental).

In denser media, liquids for example, phenomena arise moreover due to the intramolecular action and to collisions. In effect, the diffusing power of each molecule, that is to say the amplitude of the induced electric moment, varies according to the relative positions of the ions and atoms of the liquid. The movements of neighbouring molecules cause variations, continuous but relatively slow, in the molecular moment, direct collisions cause sudden changes. The representation of these variations by a Fourier series shows that the phenomenon is equivalent to a symmetrical spreading of the fundamental line or more exactly to the appearance of a continuous spectrum on each side of this line The less dispersed lines caused by the natural frequency of rotation of the molecules are thus swamped in this continuous spectrum.

If, now, we try to evaluate the light diffused by the *whole of the molecules* of the medium, and if we go back for this to formula (4), we see that the fundamental line ω, which provides for the constant part $\bar{a}_p$ of the molecular moment, is governed solely by the relative position of the molecules; its intensity will be proportional to the mean square of the changes in density.[3] On the contrary, the phases of the secondary vibrations contain the terms ϕ which vary *at random* from one molecule to another; these phases are, therefore, distributed at random; the corresponding waves are incoherent and the intensity of the secondary lines is in consequence proportional to the number of these small waves, that is to say, to the number of the diffusing molecules, whatever may be the changes in density.

We have, therefore, a means of altering the importance of the pure diffusion with regard to effects of pulsations; thus at the critical point the light due to opalescence will be solely constituted of the fundamental line, without broadening or change of wave-length; *at the critical point the effect of the pulsations becomes negligible and there is pure diffusion.*

The total radiation which constitutes the diffused spectrum of a diatomic molecule can be calculated in the ideal case of a frequency of rotation n_1 and a frequency of pure vibration n_2.

The results are given in Table I.

It has been assumed that the incident light vibrations are directed along *Oz* (Fig. 1). In these formulæ, λ signifies the wave-length of the *incident light in vacuo;* ν, the number of molecules per c.c.; δ, the molecular

[3] A. Bogros and Y. Rocard, *J. Physique*, 10, 72-77 (1929).

anisotropy [4]; $\left(\frac{\Delta r}{r}\right)^2$ represents the mean square value of the relative variation of the distance between two vibrating centres of the molecules; σ and τ are two coefficients which depend on the configuration of the molecule; in the simple case examined here, they are respectively 3 and 12. The others are standard notation.

TABLE I.

Wave-Length.	Polarised Intensity along Oz.	Polarised Intensity along Ox.
λ	$a_z = \frac{\pi^2}{\lambda^4}(\mu^2 - 1)^2 \frac{RT\beta}{N}$	$a_x = 0$
λ	$b_z = \frac{\pi}{\lambda^4 n}\frac{\delta^2}{5}(\mu^2 - 1)^2$	$b_x = \frac{3}{4}b_z$
$\lambda/\left(1 \pm \frac{2\alpha}{\omega}\right)$	$c_{1z}, c_{2z} = \left(1 \pm \frac{2\alpha}{\omega}\right)^4 \frac{\pi^2}{\lambda^4 n}\frac{3\delta^2}{10}(\mu^2 - 1)^2$	$c_{1x}, c_{2x} = \frac{3}{4}c_{1z}, c_{2z}$
$\lambda/\left(1 \pm \frac{s}{\omega}\right)$	$d_{1z}, d_{2z} = \left(1 \pm \frac{s}{\omega}\right)^4 \frac{\pi^2}{\lambda^4 n}\frac{(\mu^2 - 1)^2}{4}\tau^2\delta^4\left(\frac{\Delta r}{r}\right)^2$	$d_{1x}, d_{2x} = 0$
$\lambda/\left(1 \pm \frac{s}{\omega}\right)$	$e_{1z}, e_{2z} = \left(1 \pm \frac{s}{\omega}\right)^4 \frac{\pi^2}{\lambda^4 n}\frac{(\mu^2 - 1)^2}{20}\sigma^2\delta^2\left(\frac{\Delta r}{r}\right)^2$	$e_{1x}, e_{2x} = \frac{3}{4}e_{1z}, e_{2z}$
$\lambda/\left(1 \pm \frac{2\alpha \pm s}{\omega}\right)$	$f_{1z}, f_{2z}, f_{3z}, f_{4z} = \left(1 \pm \frac{2\alpha \pm s}{\omega}\right)^4 \frac{\pi^2}{\lambda^4 n}\frac{3(\mu^2 - 1)^2}{40}\sigma^2\delta^2\left(\frac{\Delta r}{r}\right)^2$	$f_{1x}, f_{2x}, f_{3x}, f_{4x} = \frac{3}{4}f_{1z}, f_{2z}, f_{3z}, f_{4z}$

The diffusion spectrum described is the most simple possible; but it already contains eight secondary lines $N \pm 2n_1$, $N \pm n_2$, $N \pm 2n_1 \pm n_2$ of which the table gives the intensity and depolarisation. The successive lines of the table give :—

1. The diffusion (a) corresponding to an induced moment of constant amplitude; it is derived entirely from changes in density; it is given by the Einstein-Smoluchowski formula; it is completely polarised.

2. The diffusions (b) and (c) derived from the changes in orientation of the molecules which are supposed to be now deformable; the depolarisation is $\frac{3}{4}$ in polarised incident light and $\frac{6}{7}$ in natural incident light.

3. The diffusion (d) derived from the changes in refractivity of the oscillating molecules; it is completely polarised.

4. The diffusions (e) and (f) derived from the changes in the anisotropy of the oscillating molecules; here the depolarisation is again $\frac{3}{4}$ or $\frac{6}{7}$ according to whether the incident light is polarised or natural.

Each secondary line $N \pm n_2$ is composed of the two terms (d) and (e) : its depolarisation varies therefore between 0 and $\frac{3}{4}$ (or $\frac{6}{7}$) depending on the relative importance of these two terms.

2. Control Experiments on the Theory of Optical Pulsations.

The first observations of the Raman effect quickly showed the inadequacy of the foregoing theory. Indeed the ratio between the intensity of a positive secondary line $N + n$ and the intensity of the corresponding negative line $N - n$ is on the above theory $\left(\frac{N+n}{N-n}\right)^4$; a λ^{-4} law is

[4] See *La diffusion moléculaire de la lumière*, p. 250, *et seq.*

obtained ; *the positive line should, therefore, be the more intense. But it is the contrary which always occurs* : the positive line is always less intense than the corresponding negative line and the ratio of intensity decreases very quickly as n increases. Daure has verified in a precise way that this ratio is equal to $\epsilon^{-\frac{hn}{kT}}$ (h = Planck's constant ; k = Boltzmann's constant ; T = absolute temperature), and Daure's result, inexplicable by the wave theory of light, is immediately explained, as we shall see later, by the theory of light quanta.

Thus the undulatory interpretation of the Raman effect is abandoned from the beginning, without seeking to ascertain whether, among the foregoing theoretical results, there is anything to be saved. But *on condition that the negative lines only are considered*, we find the wave theory explains certain experimental results which the theory of light quanta in its simple form appears to be unable to explain. The first point in question is the *intensity of the negative* lines. Careful measurements have been made *independently* by Daure and by Landsberg and Leontowitch.

1. The ratio between the intensity of a negative line n and that of the fundamental line diffused without change of wave-length must, theoretically, vary as $\left(\frac{N-n}{N}\right)^4$ when the fundamental line is displaced in the spectrum. Assume $n = 50$ waves per mm., and take successively $N = 2500$ (violet) ; 2000 (yellow-green). The ratio $\left(\frac{N-n}{N}\right)^4$ changes from 0·92 to 0·90. This relatively small effect is in accordance with the experimental results of Daure who has verified that, in liquids, the ratio between the intensity of a Raman line and that of the fundamental line remains practically constant over the whole of the visible spectrum.

2. On the other hand, Landsberg and Leontowitch find, between a negative line of quartz ($n = 465$ waves per cm.) and the fundamental line, the ratios of intensity which are given in Table II.

TABLE II.

Wave-length of fundamental line in Å	4047	3650	3130-3126	2654
Ratio of intensity	0·43	0·42	0·48	0·49
These ratios vary in the same sense as $\left(\frac{N-n}{N}\right)^4$.				
$\left(\frac{N-n}{N}\right)^4$	0·93	0·93	0·94	0·95

The λ^{-4} law is, therefore, applicable to the negative secondary rays as well as to the fundamental ray. Now we know the origin of this law of variation in the electromagnetic theory of Maxwell and Lorentz ; it expresses the fact that an electric oscillator of high natural frequency is put into forced vibration under the action of an alternating field of lower frequency.

Another remarkable fact, which appears hard to explain by the theory of light quanta, has been obtained by Wood with HCl gas. The fundamental line $\lambda = 4358$ Å. is accompanied, in the diffusion spectrum, by satellite negative lines which appear to be caused by the molecular rotation : these lines correspond with the rotational lines found by Czerny in the infra-red spectrum between 40 and 100 μ, but, *in the Raman spectrum, we only find one line out of two.* The lines in question in order of wave-length are given in Table III.

TABLE III.

Czerny.		Wood.		
Number of Order.	*Wave-length.*	*Wave-length.*	*n*	*Number of Order.*
$k = 11$	$\lambda = 44{\cdot}1\mu$	$\lambda = 43{\cdot}6\mu$	229 cm.$^{-1}$	$k = 7$
10	$48{\cdot}5\mu$	—	—	—
9	$53{\cdot}8\mu$	53·9	185	5
8	$60{\cdot}4\mu$	—	—	—
7	$68{\cdot}9\mu$	67·1	149	3
6	$80{\cdot}4\mu$	—	—	—
5	96μ	90 (doubtful)	111	1

This peculiar disappearance of one line out of two in the Raman spectrum is easily explained by the theory of optical pulsations. Thus, while the infra-red selective absorption spectrum gives the rotation frequency n, the optical pulsation causes the double frequencies $2n$ to occur, as our table of diffusion lines showed. This fact is easily accounted for by observing that a molecule with isotropic axis (like the molecule of HCl) revolving round a line perpendicular to this axis returns to its initial state after *half a rotation.*

To be more precise, let

$$E = \frac{h^2}{8\pi^2 I} k(k-1) \quad (\text{where } k = 1, 2, 3 \ldots \; I = \text{moment of inertia})$$

represent the energy levels of a rotating molecule, such as the heteropolar molecule HCl. The frequency ν_k of an infra-red absorption line is given by the relation

$$h\nu_k = E_{k+1} - E_k = \frac{h^2}{8\pi^2 I} \cdot 2k$$

whence

$$\nu_k = \frac{h}{4\pi^2 I} \cdot k.$$

But the energy E_k is that of a molecule which turns with a frequency of rotation n_k given by the formula,

$$E_k = 2\pi^2 I n_k^2$$

whence we obtain

$$n_k = \frac{h}{4\pi^2 I} \cdot \sqrt{k(k-1)}.$$

The frequencies n_k of the rotating molecule defined by the classical theory are thus practically equal to the infra-red frequencies ν_k, provided k is large enough, and the intervals $2n_k$ between two secondary bands of the diffusion spectrum are twice as large as the intervals ν_k between two infra-red bands.

3. Interpretation of the Raman Effect by the Theory of Light Quanta.

Certain relationships anticipated from theory of optical pulsations are, thus, found to be verified experimentally when the negative bands alone are considered. But this remarkable result, which is certainly due to a still obscure law of correspondence, does not, however, justify the classical undulatory view-point.

I have shown elsewhere [5] that at ordinary temperature, there is only one molecule of methane in vibration amongst 250,000 molecules at rest. At the temperature of liquid air the number of vibrating molecules is naturally still smaller. Now Daure has shown that liquid methane at a temperature of — 180° C., emits strongly the negative secondary line $n = 2908$ cm.$^{-1}$. This line is not then a line of pulsations produced by the vibrating molecules: its intensity would be inexplicable. It is necessary to admit that the *molecules* which diffuse this Raman line *are set into vibration by the incident light*, and that is a different matter.

In the theory of optical pulsations, the incident wave does not give energy to the molecule; all the energy is re-emitted by diffusion. But, in actual fact, a portion of the incident energy is given to the molecule which passes to a higher energy level; *there is true absorption.* The theory of light quanta must, therefore, be used, since this governs the exchange of energy between light and matter.

Light is propagated with a finite speed. What happens to the energy from the moment at which it leaves the source and that when it reaches the receptor? What happens to the principle of the conservation of energy? Formerly this energy was assumed to be in a hypothetically continuous medium, the *ether.* To-day, we prefer to assume the existence of particles of energy, *light quanta* associated with waves which are propagated *in vacuo* with a speed of 3×10^{10} cm./sec. and each carrying a quantity of energy

$$W = hN$$

(h = Planck's constant; N = frequency of the associated wave train).

Let us suppose that the quantum, falling on a molecule, alters the energy level of the molecule, and that this level passes from E_1 to E_2. The energy of the diffused quantum is only

$$W' = hN' = hN - (E_2 - E_1)$$

and the corresponding frequency

$$N' = N - \frac{E_2 - E_1}{h}.$$

The quantity $E_2 - E_1/h$ is one of the *emission or absorption frequencies* of the molecule under consideration. If $E_2 > E_1$, the energy of the molecule is increased; the energy of the quantum, decreased; and the frequency of the diffused radiation $N' = N - n$, is less than that of the incident light. This is the Raman effect.

In this theory the frequency of a radiation must change every time it exchanges energy with particles of matter. Now it is not very probable that a beam of light will pass through a material medium without acting more or less on it, that is to say without the frequency of the radiations being more or less altered. In general, *under ordinary physical conditions*, the light quanta are deranged by the molecules of matter, partitioned into quanta of lesser frequency, and certain of them are found to be definitely absorbed by the medium; all these phenomena correspond to a *degradation of the light frequencies.*

The frequencies of the radiations emitted by the material medium are, collectively, lower in frequency than the exciting radiation because the material absorbs more energy than it re-emits. This is the meaning of the old Stoke's law, which is only a particular case of the degradation of luminous frequencies by matter.

[5] J. Cabannes, *J. Physique*, 6, 196 (1925).

Whenever there is a degradation of frequency, the classical Fresnel-Maxwell-Lorentz undulatory theory is certainly inadequate. This is the case in the Raman effect where the secondary negative lines are more intense than the positive lines. We must, therefore, introduce light quanta in the explanation of the Raman effect, though, in its present state, this new theory does not appear to be completely capable of explaining all the observed facts.

4. Classification of the Different Phenomena which give rise to a Degradation of Frequency.

We can enumerate and classify quite rapidly the phenomena in which light quanta give energy to material particles.

(1) In *the photoelectric effect* the incident quantum is totally absorbed; part of the quantum of energy provides the work necessary to tear the electron from the atoms and molecules of the medium; the remainder is not radiated again; it sets the electron in movement.

(2) In *fluorescence* there is also total absorption of the incident quantum W; a part w of the energy is used in increasing the energy level of the molecule; the remainder increases the thermal agitation of the medium. The return of the molecule to its normal state will be accompanied by the emission of light of frequency $n = \frac{w}{h} < \frac{W}{h} = N$. This is Stokes' law, one of the oldest aspects of frequency degradation.

3. But things can happen otherwise. If the quantum $W = hN$ encounters a *free* electron at rest, it will shoot it out with a certain velocity and will itself rebound with a decreased energy $W' = hN'$; this is the *Compton effect.* Here a part of the incident energy is radiated again.

4. If the quantum meets a more complicated material system (ions, atoms, molecules) it can, in certain cases, raise the energy level of the system, which absorbs part (w) of the incident energy W. The rest $w' = W - w$ is diffused with a lower frequency: this is the *Raman effect.*

This tabulation shows plainly the essential difference between the Raman effect and the phenomena of fluorescence (or of resonance). In fluorescence, the frequency of the re-emitted light (n) is directly associated with the natural frequencies of the fluorescent medium; in the Raman effect it is the difference $N - N' = n$ between the exciting frequency N and the emitted frequency N' which corresponds with the natural frequencies of the substance; *a Raman spectrum is in reality an absorption spectrum.*

It now remains to interpret those facts which deviate from Stokes' law. These facts show that a particle can radiate more energy than it could have received by absorption of the incident quantum. In the Raman effect the existence of a positive line can be explained by the return to a normal state, under the action of the incident quantum, of molecules previously at a higher energy level. The intensity of these positive bands (anti-Stokes) should, therefore, increase rapidly with temperature, at the same time as the number of molecules possessing excess energy or rotation or vibration, increases.

5. Enumeration of the Experimental Results relative to the Degradation of Frequencies in the Molecular Diffusion of Light.

If a homogeneous medium (amorphous or crystalline) is illuminated by monochromatic light of frequency N_1 the molecular diffusion of the incident light is accompanied by the following three effects :—

(1) The appearance, in the diffused light, of secondary positive and negative lines of frequencies $N + n$, the increase or decrease in frequency n being independent of the incident light and associated directly with the natural frequencies of the medium.

(2) The appearance of a continuous spectrum over an interval capable of extending for 50 Å., on each side of the fundamental line.

(3) Unsymmetrical broadening of the fundamental line.

With each of these three effects, we find a degradation in frequencies. In the course of this paper, I have reviewed, discussed and interpreted the experimental results obtained up to the present by Daure and myself with regard to this degradation of frequency.

6. Ratio of the Intensities of the Positive and Negative Lines.

Let I_+ and I_- be the intensities of two symmetrical lines $N + n$ and $N - n$. In the theory of optical pulsations this ratio is equal to $\left(\frac{N+n}{N-n}\right)^4$, that is, the positive line is always the more intense. But experiment shows that *the intensity of a positive line is always less than that of the corresponding negative line ; more especially is this the case when the increase of frequency is greater* (see Plate A).

Again Daure has found that the intensity of the lines $\pm$ 15 mm.$^{-1}$ of $AsCl_3$ were in the ratio 0·4, that of the lines $\pm$ 19 of PCl_3, in the ratio 0·3 ; and those of the lines $\pm$ 39·5 of $AsCl_3$ in the ratio 0·1. On the other hand the lines $\pm$ 99 of benzene appear to have a ratio of 0·01. While though the line — 306 of benzene is very intense, the positive line + 306 has never been observed.

It seems that *the ratio I_+/I_- is strictly independent of* the nature of the diffusing medium and varies very nearly as

$$r = e^{-\frac{h\nu}{kT}},$$

(h and k Planck's and Boltzmann's constants respectively; T absolute temperature ; ν frequency expressed as number of cycles per second). We have at 300° K, $\frac{h}{kT} = 0{\cdot}17 \times 10^{-12}$. If we wish to express the frequency in waves per millimetre, we must multiply this coefficient by 3×10^{11}, which gives

$$r = e^{-0{\cdot}051n}.$$

Examples :—

$n = 10$	20	50	100	300
$1/r = 1{\cdot}67$	2·78	12·8	165	4,480,000

We see that it is very difficult to observe positive lines with a frequency greater than 100.

Daure has compared, by an accurate photometric method, a dozen

positive lines with their corresponding negative lines, and he has verified with great accuracy the exponential law, $r = e^{-An}$. If $A = \frac{hc}{kT} = \frac{hcN}{RT}$ we have for determining Avogadros' number N an optical method which is much more precise than that utilising diffusion without change of wave-length and the well-known formula of Lord Rayleigh. M. Daure found $N = 6{\cdot}6 \times 10^{23}$.

Raman was the first to be able to interpret the rapid decrease in intensity of the positive lines as the frequency n increases. Let E_0 be the energy level of the molecule in its normal state, E_n the level (higher) of which the return to its normal state corresponds with the emission of frequency n. We have

$$hn = E_n - E_0 = \Delta E.$$

The number of molecules which happen to be on an energy level E_n is, moreover, proportional to $e^{-\frac{\Delta E}{kT}}$. If we admit that the probabilities of the two changes $E_0 - E_n$ and $E_n - E_0$ are the same, under the action of an incident quantum, the ratio of the intensities I_+/I_- is equal to the ratio between the number of molecules which happen to be in the state E_n and that of the molecules in the state E_0, that is

$$e^{-\frac{\Delta E}{kT}} = e^{-\frac{hn}{kT}}.$$

In actual fact, the circumstances are a little more complicated. If we imagine only linear oscillators, the energy levels are, it seems,

$$E_p = (p + \tfrac{1}{2})h\omega \qquad (p = 0, 1, 2, 3 \ldots)$$

ω designating the oscillation frequency defined by classical theory. The same positive line $n = q\omega$ is, then, given by all the transformations

$$\Delta E = E_{p+q} - E_p = qh\omega$$

(q being a whole number). The number of molecules which could undergo these transformations is proportional to

$$\sum_{p=0}^{p=\infty} e^{-E_{p+q}/kT}.$$

Similarly the negative line is given by all the transformations

$$-\Delta E = E_p - E_{p+q} = -qh\omega.$$

The number of molecules which can undergo these transformations is proportional to

$$\sum_{p=0}^{p=\infty} e^{-E_p/kT},$$

whence the ratio of intensities is

$$\frac{I_+}{I_-} = \frac{\Sigma e^{-E_{p+q}/kT}}{\Sigma e^{-E_p/kT}} = e^{-\frac{qh\omega}{kT}} = e^{-\frac{hn}{kT}}.$$

We obtain the same ratio as in the simple hypothesis of Raman. An inexplicable fact remains however; how is it that the probability of two inverse transformations, one with absorption of energy, the other with emission of energy, should be the same, under the impact of a quan-

tum of light? According to Daure's measurements, however, we shall obtain experimental proof.

7. Want of Symmetry between the Positions of the Positive and the Negative Lines.

We have admitted that the frequencies of two corresponding secondary lines, positive and negative, are $N + n$ and $N - n$, where N is any frequency of the exciting radiation. That is to say that in the frequency scale, the positions of the secondary lines are symmetrical with respect to the fundamental line.

I have proved that this is not strictly true. The frequencies of the secondary lines are $(N - \epsilon) \pm n$. There is, therefore, a displacement towards the red, *i.e.* a further degradation in frequency. Thus, in quartz and Iceland spar, for example, measuring the changes in frequency (for the mercury line 4358·34 Å.) :

Quartz	− 12·85 ± 0·05	and + 12·75 ± 0·05	waves per mm.
Spar	− 15·67	„ + 15·39	„ „ „
	− 28·32	„ + 27·97	„ „ „

In quartz each line appears displaced by $\epsilon = 0{\cdot}05$ mm.$^{-1}$ ($\Delta\lambda = 0{\cdot}1$ Å. approx.) ; in spar, by $\epsilon = 0{\cdot}15$ mm.$^{-1}$ ($\Delta\lambda = 0{\cdot}3$ Å. approx.).

These measurements are delicate since the lines are always rather wide, even in crystals. Thus the line ± 28 mm.$^{-1}$ of Iceland spar is 3·5 Å. wide. The wavelengths are determined by photographic comparison with the neighbouring lines of the iron arc. The accuracy of the results depends greatly on the time of exposure chosen ; it is, above all, necessary to avoid over-exposing the lines to be studied. These measurements have been made on the beautiful plates of Daure.

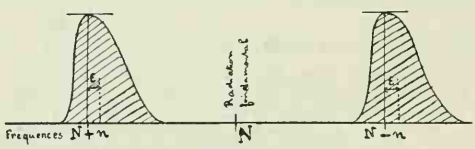


FIG. 2.

This displacement towards the red reveals without doubt an unsymmetrical broadening analogous to that which I have observed in the case of liquids for the fundamental line, and which will be described later. Fig. 2 shows this phenomenon.

8. Experimental Study of the Continuous Spectrum on Both Sides of the Fundamental Line.

Thanks to the very clear spectroscope constructed by Daure for the study of the resonance of bromine vapour, we have been able to reproduce the Raman effect at Montpellier very easily and to discover the fundamental laws concerning it. But our spectra show in addition a considerable broadening (nearly symmetrical) of the mercury lines in diffusion in benzene and ether. The following results refer to the line 4358 Å. :—

		Distance from the Centre of the Line (in Å.).			
		4.	8.	12.	16.
Relative intensity .	Benzene	400	80	25	8
	Ether	20	4		

With a sufficiently long exposure benzene gives on each side of the position 4358 Å. a true band continued for a total interval of 50 Å.

In reality this continuous spectrum is not symmetrical on each side of the incident line ; it is prolonged a little further towards the red than towards the violet. This dissymmetry has lately been recognised by Raman and measured by Gerlach ; it can hardly be observed in the case of the line 4358 because of the two satellites 4347 and 4339 which obscure the phenomenon towards the short wave-lengths, but, in the case of the line 4047, Gerlach finds a broadening of 38 Å., with 22 Å. towards the red and 16 towards the violet.

In crystals of sodium chlorate, Iceland spar and quartz the same continuous spectrum is found, which extends unsymmetrically on both sides of the fundamental line. The intensity of the spectrum does not decrease slowly at the sides ; on the contrary, a sharp fall in intensity is observed which gives very clean edges easy to determine. Thus, in the three crystals studied the continuous spectrum excited by the line 4358 stops abruptly exactly at the same place, at 19 Å. towards the red from the fundamental.

9. Unsymmetrical Broadening of the Incident Radiation by Molecular Diffusion at the Middle of a Gas or Liquid.

A fact, distinct from the foregoing and not less curious is the change in the fine structure of a monochromatic exciting line by molecular diffusion. It is not a matter here of changes easy to demonstrate with a prism spectroscope or a grating, but of variations which are very small and the study of which demands the employment of the methods of interference spectroscopy.

The apparent change of wave-length effected by the diffusion of light in the middle of a gas was the first case of the degradation of frequency observed in molecular diffusion. By illuminating a Pérot and Fabry interference standard with the mercury line 4358 Å. diffused by butane at normal pressure (butane is one of the gases which diffuse the most light), I have been able to photograph the interference rings. The apparatus is shown in Fig. 3. The primary beam $x'ox$ is propagated in the focal plane of an achromatic lens L_1. The diffused beam passes through this lens, then the étalon P.F., and forms an image of the primary beam at the focus ϕ of a photographic objective L_2 opened wide. If a vessel containing quinine is interposed at C, only the group of radiations 4358 Å. effects the sensitive plate and, if the thickness of the étalon is well chosen, at the image of the primary beam there are superimposed interference rings of which the comparative diameter can be measured.

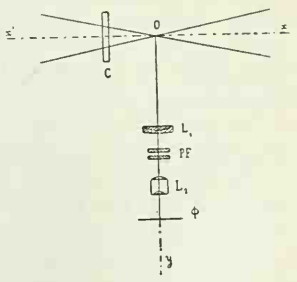


Fig 3.

The difficulty arises from the fact, that, to obtain interference rings with the large separation chosen (thickness of étalon 10 mm.), the lamp must be kept low, which decreases the brilliance considerably.

Two exposures are made on the same plate, one after diffusion from a solid matt surface composed of very small grains (velox photographic paper, blackened by developing and fixing), the other after diffusion through butane.

With the solid diffused the length of exposure is a fraction of a second,

but with gas it must be exposed for thirty hours, which necessitates an étalon with invar blocks. On development, the image caused by the butane appears first, but it stops quickly ; the image due to the velox paper, slower in appearance, always ends by reaching the same depth as the first, or even exceeding it ; it seems that the feeble light diffused by butane only affects the surface of the plate.

Also, the rings are sharper and easier to measure when they are obtained by short exposures with velox paper. The two systems of rings are not very comparable.

Four passable measurements have been made under these conditions ; they are given in Table IV.

TABLE IV.

Diameter of the First Ring in mm.	
Butane.	*Velox Paper.*
0·503	0·523
0·485	0·507
0·474	0·509
0·480	0·505

Thus, the diameter of the rings is a little smaller with butane, which corresponds with an apparent increase in wave-length of about 0·01 Å. The broadening reaches 0·04 Å. approximately.

Preliminary measurements, which were much easier, were made with an interference étalon 15 mm. thick, and showed that the radiations of the group 4356 Å. keep the same wave-length, to about 0·001 Å., both after reflection from a glass, silver, gold or fuchsin mirror and after diffusion from any solid surface (porcelain, wood, paper).

With liquids which diffuse more light, the measurements are much easier than with gases : by reason of shorter time of exposure, and photographic objective of greater focal length (which gives rings larger and easier to measure). We find a greater apparent broadening and displacement than the foregoing (see Plate B.).

In the first place an étalon 10 mm. thick does not give rings, a proof of a more considerable enlargement.

So we have studied the light diffused laterally by liquids with an étalon of half the thickness. Beautiful rings are then obtained with the vibration *I* (normal to the incident ray) : they are not obtained with the vibration *i* (parallel to the incident ray). It follows that the changes in orientation of the anisotropic molecules (which are only responsible for the term *i*) emit by diffusion a line too large to give rings in an étalon 0·5 mm. thick. The radiation of intensity *I* (where the changes in orientation play only a small part) are, however, enlarged (enlargement $< 0{\cdot}1$ Å.) and displaced towards the red. This displacement is about 0·05 Å. and varies little from one liquid to another.

Methyl alcohol	= 0·065 Å.	Acetic acid	= 0·055 Å.
Ethyl ,,	= 0·050	Cyclohexane	= 0·060
N. Propyl. ,,	= 0·070	Benzene	= 0·035
		PBr_3	= 0·055

These changes must not be confused with the appearance, mentioned above, of a continuous spectrum on both sides of the fundamental line. The total intensity of the light in this spectrum, which does not reach one-tenth of the intensity of the fundamental line, does not interfere with the observation of the interference rings.

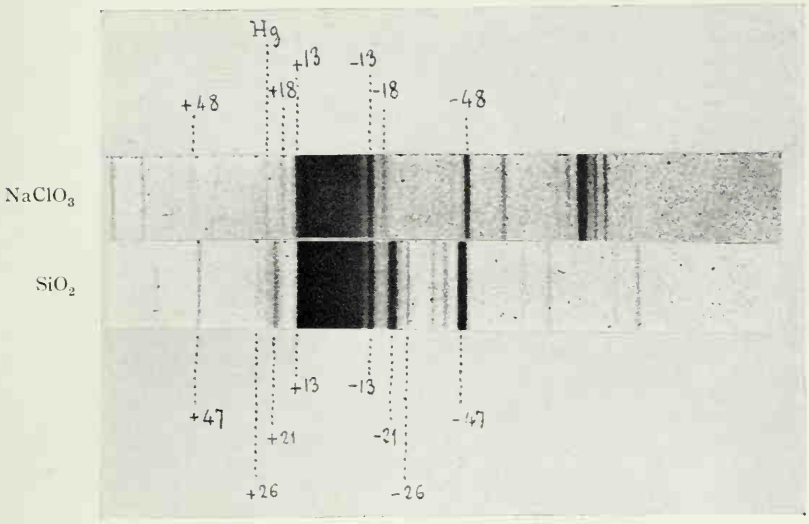


PLATE A.—Positive and negative rays of $KClO_3$ in quartz.

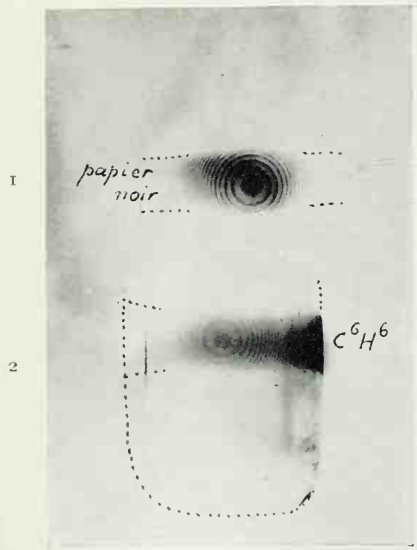


PLATE B.—Interference ring obtained with a Pérot and Fabry étalon, 5 mm. thick.
1. Mercury radiation 4,358 Å diffused by a matt solid surface.
2. Same radiation diffused by benzene.

PLATE A.

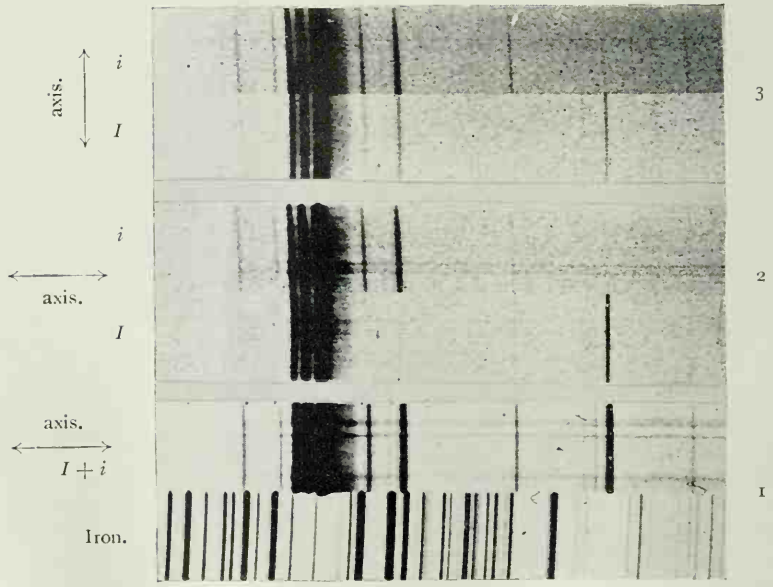


PLATE B.—ICELAND SPAR.

[*Cabannes—Polarisation of Raman Radiations.*] [*To face page* 813.

The displacement towards the red is observed also in the light diffused by vitreous solids (metastyrolene). As yet no measurements have been possible in crystals because the intensity of the molecular diffusion is very feeble and almost always hidden by stray diffusion.

These results are opposed to those of Rocard and Bogros who have obtained in critical opalescent light neither broadening or displacement. They have arrived at the same negative conclusion with the resonance light of sodium vapour. However, one does not very well see how the diffused light which results from changes in density could be modified; the theory of optical oscillations has shown that this diffusion corresponds with the *constant* portion of the amplitude of the molecular moments, which is in accordance with the results of Rocard and Bogros on critical opalescence.

We must admit that there exist fluctuations other than fluctuations in density which diffuse strongly polarised light. The importance of the diffusion which results from these fluctuations would be, for ordinary liquids, of the same order as that from fluctuations in density, whereas at the cr tical point the changes in density become sufficiently important to mask all other causes of diffusion. The nature of these hypothetical fluctuations remains to be determined.

POLARISATION OF RAMAN RADIATIONS IN LIQUIDS AND CRYSTALS.

By Professor J. Cabannes.

Received in French, 19th June, 1929, and translated by A. F. Weiss, B.Sc., A.I.C.

1. General.

Amongst the most interesting and important results relating to diffusion spectra, mention must first be made of those which concern the state of polarisation of the secondary radiations:

All the secondary radiations (negative or positive), characterised by the same change of frequency $\pm n$, *are in the same state of polarisation, whatever the frequency N of the exciting radiation. This state of polarisation, moreover, varies within wide limits, according to the pair of secondary radiations* $\pm n$ *under consideration.*

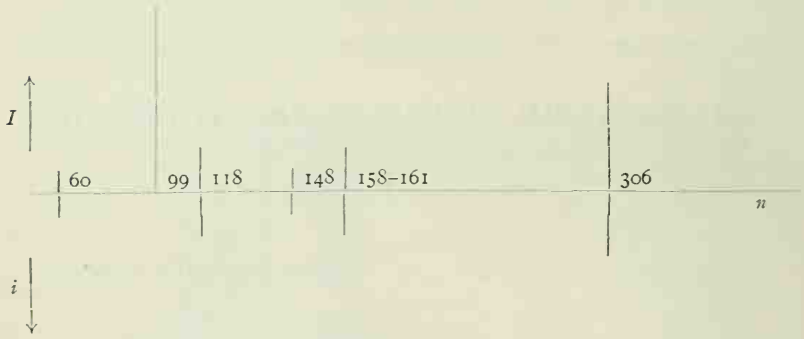
Let us now recall the so-called " Depolarisation factor " in the study of the diffusion of a beam of natural light by a fluid. When one considers the light diffused at 90° to the incident beam, it is the ratio between the intensity i relative to the vibration parallel to the incident ray, and the intensity I relative to the vibration perpendicular to this ray. The depolarisation ρ of the radiations diffused without change of wavelength remains practically constant throughout the spectrum. It depends essentially on the anisotropy of the molecules and on the importance of the diffusion produced by the fluctuations in density in relation to that produced by the fluctuations in anisotropy. If fluctuations in density alone are in question, ρ is zero; if the diffusion produced by

the fluctuations in density is negligible in comparison with the other source of diffusion, ρ can be as great as $\frac{6}{7}$.

2. Representation of Diffusion Spectra.

Diffusion spectra can be represented in a fairly complete manner by graphs which indicate at the same time the *frequency* of the different secondary radiations, their *intensity*, and their *depolarisation*. The changes in frequency n, starting from the fundamental radiation, are set out on a horizontal axis, taking into consideration only the negative radiations, since the properties of the positive radiations (intensity and depolarisation) can be at once derived from them. Each secondary radiation is then represented by a straight line perpendicular to the axis of frequencies, the length above this axis being proportional to I, and the length below the axis to i. Here, for instance, is the Raman spectrum of benzene. The graph represents the following results :

Benzene									
Frequency* . .	n	0	60	99	118	148	158-161	306
Intensity . .	$I + i$	1000	4	18	6	4	6	12
Depolarisation .	$\frac{i}{I}$	0·42	1	0·04	1	1	1	0·6



Raman Spectrum of Benzene (negative radiations).

The depolarisation of secondary radiations has been studied in a certain number of liquids and in two crystalline substances, quartz and Iceland spar.

3. Depolarisation of Light in Liquids.

The first measurements were made on benzene and ethyl ether, the two liquids which have been the most thoroughly investigated from the point of view of molecular diffusion. It is known that ether is composed of optically isotropic molecules : the light which it diffuses is very much polarised ($\rho = 0{\cdot}085$) ; benzene is formed of anisotropic molecules : it diffuses three times as much light as ether, and this light is much more depolarised ($\rho = 0{\cdot}42$).

In order to measure the depolarisation[1] of the Raman radiations, the light from a mercury arc was concentrated in the liquid. The diffused light illuminated a vertical slit which was projected by means of a

(*n in the first line of the table is expressed in wave-numbers per millimetre.)

[1] J. Cabannes, *Comptes Rendus*, **187**, 654 (1928).

quartz-fluorite lens on to the horizontal slit of a quartz spectrograph, after separating with a Wollaston prism the two images corresponding to the vibration I (normal to the incident beam and diffused) and to the vibration i (parallel to the incident beam). A double spectrum was thus obtained. Each negative included a series of double spectra obtained with times of exposure comprised between 30 minutes and 73 hours. For the purpose of tabulating results, the depolarisation of the radiations diffused without change of wave-length has been supposed to be known, and the γ of the plate has been considered to be constant in a spectral interval of some hundreds of Ångströms (γ is the ratio between the variation in optical density of the negative, and the variation in the ogarithm of the illumination).

In Table I., for instance, are the results of measurements on benzene.

TABLE I.—Benzene.

Wave-Length in Å.		Number of Waves per Millimeter.		Observations.
Mercury Radiations.	Secondary Radiations.			
$\lambda_1 = 3126$		$N_1 = 3199$		
$\lambda_1 = 3126$	3231	$N_1 - n = 3100$	$n = 99$	$\rho \leq 0{\cdot}035$.
$\lambda_2 = 3341$		$N_2 = 2992$		
$\lambda_2 = 3341$	3457	$N_2 - n = 2893$	$n = 99$	Confused together on the negative.
$\lambda_1 = 3126$	3462	$N_1 - n = 2893$	$n = 306$	
$\lambda_3 = 3650$		$N_3 = 2739$		
$\lambda_2 = 3341$	3672	$N_2 - n = 2686$	$n = 306$	Hidden by the enlargement of the preceding radiation.
$\lambda_3 = 3650$	3787	$N_3 - n = 2640$	$n = 99$	Badly separated from a neighbouring mercury radiation.
$\lambda_4 = 4047$		$N_4 = 2471$		
$\lambda_3 = 3650$	4110	$N_3 - n = 2433$	$n = 306$	Hidden by the enlargement of the preceding radiation.
$\lambda_4 = 4047$	4215	$N_4 - n = 2372$	$n = 99$	$\rho \leq 0{\cdot}035$.
$\lambda_5 = 4358$		$N_5 = 2294$		
$\lambda_5 = 4358$	4555	$N_5 - n = 2195$	$n = 99$	$\rho \leq 0{\cdot}035$.
$\lambda_4 = 4047$	4619	$N_4 - n = 2165$	$n = 306$	$\rho = 0{\cdot}6$.
$\lambda_5 = 4358$	4683	$N_5 - n = 2135$	$n = 159$	$\rho = 1$.
4916				
$\lambda_5 = 4358$	5030	$N_5 - n = 1988$	$n = 306$	$\rho = 0{\cdot}6$.

Thus, the two most intense lines of the diffusion spectrum of benzene, $n = 99$ and $n = 306$, give $\rho \leq 0{\cdot}035$ and $\rho = 0{\cdot}6$, whilst, in the case of the ordinary diffusion, it is found that $\rho = 0{\cdot}42$.

The change in the depolarisation factor is shown in a striking manner by the negatives which served for the preceding measurements: the 4 radiations $n = 99$ excited by the mercury radiations 3126, 3650, 4047, and 4358 Å., only appear in the spectrum I, whilst the mercury radiations themselves, and the two radiations $n = 306$, excited by the radiations 4047 and 4358 Å., appear in the two spectra I and i.

Another series of measurements made with a glass spectrograph of greater dispersion gave the figures shown in Table II.

These results agree fairly well with those in Table I.

Naturally if, instead of illuminating the liquid by natural light, a luminous vibration is sent into it *parallel to the direction in which the diffused light is observed*, the depolarisation factor becomes equal to 1

for all the diffused radiations. Nothing now distinguishes the spectra I and i from one another. The phenomenon is entirely symmetrical around the rectilinear incident vibration.

TABLE II.

$n = 61$ mm.$^{-1}$	ρ in the neighbourhood of 1
99	$\rho = 0{\cdot}04$
118	ρ in the neighbourhood of 1
148	ρ in the neighbourhood of 1
159-160	$\rho = 1$
306	$\rho = 0{\cdot}6$

With ether, the depolarisation of the strong radiation $n = 146$ mm.$^{-1}$ appears to be complete, and the group of the 3 radiations, $n = 287$, 293, 298, gives $\rho = 0{\cdot}45$, whilst the depolarisation of the radiations diffused without change of wave-length is only 0·085.

Trichloride and tribromide of phosphorus gave the figures shown in Table III.

TABLE III.

PCl_3	n	0	± 19	− 25·5	− 49
	$I + i$	1000	40	10	80
	i/I	0·2	1	0·02	0·2
PBr_3	n	0	± 11	− 15·5	± 39
	$I + i$	1000	100	25	100
	i/I	0·4	1	0·02	0·3

Table III. shows the relationship of the molecules PCl_3 and PBr_3, and the correspondence between the secondary radiations in the two spectra.

In the same manner, in the case of carbon tetrachloride, and tin tetrachloride, the strong radiations [2] which correspond to $n = 45{\cdot}7$ and $n = 36$ mm.$^{-1}$, are nearly completely polarised ($\rho = 0{\cdot}05$).

In a general way, the depolarisation of the secondary radiations varies enormously, for the same liquid, between one radiation and another. It can be smaller or larger than the depolarisation of the radiation diffused without change of wave-length, *but it is never greater than unity*. The weaker radiations are in general nearly completely polarised.

Pringsheim [3] and Raman and Krishnan [4] independently obtained similar results.

4. Coherence and Non-Coherence of Diffused Waves. Comparison of the Depolarisation of Raman Radiations in Liquids with the Depolarisation of the Fundamental Radiation in Vapours.

The light diffused by a perfect gas is easy to calculate : it is sufficient to consider the molecules as independent sources, like little stars, and to add together their luminous intensities. Everything happens as if the wavelets diffused by each molecule were non-coherent.

In dense fluids, where the molecules are no longer independent of one another, or in crystals, where they are in a regular configuration, the

[2] Daure, *Comptes Rendus*, 187, 940 (1928).
[3] *Z. Physik*, 51, 511 (1928). [4] *Proc. Roy. Soc.*, **122**, 23 (1929).

diffused light must be calculated from a consideration of the electric vectors emitted by each molecule, and the preceding result is no longer found: the intensity diffused by each cubic centimetre is no longer proportional to the number of molecules; the wavelets diffused by each molecule are coherent, and they interfere. They also interfere in the case of the perfect gases (there can be no essential difference between a gas and a liquid), but it is found that in a gas the diffused light is the same as if the wavelets were non-coherent.

These remarks will throw light on the rather obscure problem of the coherence of Raman radiations. Let us consider solely the negative radiations. Experiments have clearly shown that their intensity does not vary with fluctuations in density, but that it is proportional to the number of the molecules (Daure, Rocard, and Bogros, Landsberg and Leontowitsch). The molecules which emit a secondary radiation can therefore be considered as non-cohering sources. It does not follow, however, that there is not agreement in phase between the vibrations emitted by different molecules which have been excited by the same incident wave. It does not follow that the wavelets thus emitted are incapable of interfering. The experiments hitherto made do not allow any conclusion to be drawn as to the mechanism of the emission. These experiments prove only that the molecules which emit a certain secondary radiation are distributed entirely at random in the illuminated medium.

In any case, it would not be reasonable to compare the depolarisation of the secondary radiations with the depolarisation of the radiations diffused without change of wave-length by the substance *in the liquid state*. This was recognised by Raman,[5] and he, therefore, compared the depolarisation of the secondary radiations with that of *the fundamental radiation diffused by gases and vapours*. The theory which he outlined appears, however, to be disproved by experiment.

5. Raman's Attempt to Explain the Depolarisation of the Secondary Radiations.

The author supposes that, for a given transformation of energy ΔE (transition energy), three principle axes in the molecule can be considered, to each of which a coefficient of probability can be applied, defined as follows: the probability of the transformation ΔE under the action of an exterior force parallel to one of these principle axes is proportional to the corresponding coefficient. Without having to investigate the mechanism of the phenomenon, this assumption invokes at once a certain molecular anisotropy and a certain depolarisation of the secondary radiation relative to the transformation of energy ΔE. To explain the change in the depolarisation factor from one secondary radiation to another, it suffices to assume a change in the principle axes and in the coefficients of probability when different transformations of energy $\Delta_1 E$, $\Delta_2 E$, are considered.

The depolarisation of the secondary radiation is then calculated in the same manner as the depolarisation of the fundamental radiation is calculated in the classical theory of the molecular diffusion of light within a gas. The coefficients of probability, introduced above, take the place of the principle refractivities A, B, C.[6] The factor ρ can vary from 0 to $\frac{1}{2}$. The lower limit corresponds to perfect isotropy; the higher limit

[5] *Proc. Roy. Soc.*, **122**, 31 (1929).
[6] J. Cabannes, *La diffusion moléculaire de la lumière*, Paris (1929).

to a linear molecule. The experimental results of Raman were comprised between these limits.

As shown above, however, my own investigations gave depolarisations definitely greater than 0·5, even for intense radiations. Thus, for the 306 mm.$^{-1}$ radiation of benzene, $\rho = 0{\cdot}6$. For the $\pm$ 19 mm.$^{-1}$ radiations of PCl_3, and the $\pm$ 11 mm.$^{-1}$ radiations of PBr_3, ρ is found to be very nearly 1. Another theoretical explanation must, therefore, be found.

6. Hypothesis of a Virtual Oscillator permanently Associated with the Molecule.

Experiment shows that each molecule emits a polarised spherical wave. We can look upon this polarisation as the projection, on a plane tangential to the wave, of a certain ellipse of vibration situated at the centre of the wave, and *permanently associated with the molecule.* Without directly introducing the material oscillator of classical theory, we thus employ a virtual oscillator to define the properties of the diffused wave.

Such is the interpretation suggested by Warwilow and Lewschin, and developed by F. Perrin [7] in the case of the polarisation of fluorescence. It can be immediately applied to the Raman effect, and can be developed quantitatively without difficulty.

To each secondary radiation there corresponds an ellipse of vibration which, referred to a trirectangular trihedron $Ouvw$ associated with the molecule, has as components :—

$$u = A \sin (\alpha t + \phi)$$
$$v = B \sin (\alpha t + \chi)$$
$$w = C \sin (\alpha t + \psi).$$

The calculation is completed by introducing the orientation of the molecule with regard to the incident luminous vibration, and by taking into consideration that the probability of excitation of the molecule depends on this orientation. The molecules to which the incident quantum communicates the energy ΔE are not oriented at random, but are distributed about a definite direction. The final result of the calculation is

$$\rho = \frac{6(1 - \epsilon^2) + \epsilon^4}{7(1 - \epsilon^2) + 2\epsilon^4},$$

where ϵ represents the eccentricity of the virtual elliptic oscillator.

The depolarisation varies from $\rho = \frac{1}{2}$ ($\epsilon = 1$, circular oscillator) to $\rho = \frac{6}{7}$ ($\epsilon = 0$, rectilinear oscillator).

It is important to understand what is the essential difference between the two hypotheses of Raman and F. Perrin. In the first, the diffused wave is always emitted by a *linear* oscillator, but the orientation of this oscillator in the molecule depends on the direction of the exciting vibration with respect to the principle axes of the molecule. In the second, the diffused wave is emitted by an *elliptic* oscillator whose orientation and eccentricity are independent of the exciting vibration and are completely determined in the molecular structure.

These two extreme hypotheses lead to contradictory results, since,

[7] *J. Physique*, 7, 392 (1926).

in the first case, the depolarisation would vary from 0 to $\frac{1}{2}$, and, in the second case, from $\frac{1}{2}$ to $\frac{6}{7}$.

Neither of these hypotheses is verified by our measurements of depolarisation, since we find values of ρ sometimes very close to zero, and sometimes approximating to unity.

However, it is as well to remark that a secondary wave is not emitted by any particular oscillator within the molecule but, probably, by the molecule as a whole. The oscillator has the effect, only, *of absorbing* a small fraction of the incident energy. The incident quantum being hN, the diffused quantum $h(N\text{-}n)$ is not very different from it, *because n is always small in comparison with N*. The question arises, therefore, whether the mechanism of the emission of secondary waves is essentially different from that of waves diffused without change of wave-length.

7. Principle of Correspondence between the Depolarisation of Light in the Raman Effect and the Depolarisation of Light in the Theory of Optical Beats.

The theory of optical beats enables us to calculate the depolarisation of the two secondary radiations which are obtained by beats between the exciting wave of frequency N and the intramolecular vibration n. The following formula (for the case where the incident light is natural) is taken from the table contained in our preceding communication :—

$$\rho = \frac{6e_z}{7e_z + 4d_z} = \frac{6}{7 + 20\left(\frac{\tau}{\sigma}\right)^2\delta^2}$$

σ and τ are two parameters which vary with the molecular structure, and which have been calculated by Rocard and myself in the simple case of a diatomic molecule. It is then found that $\sigma = 3$ and $\tau = 12$, whence

$$\rho = \frac{6}{7 + 320\,\delta^2}.$$

On the other hand, the measurement of the depolarisation ρ_0 of light diffused by gases without change of wave-length gives the square of the molecular anisotropy δ^2 :—

$$\delta^2 = \frac{5\rho_0}{6 - 7\rho_0}.$$

Whence

$$\rho = \frac{6 - 7\rho_0}{7 + 258{\cdot}5\,\rho_0}.$$

Examples { Hydrogen . . . $\rho_0 = 0{\cdot}027$ . . . $\rho = 0{\cdot}104$
Oxygen . . . . $0{\cdot}064$ . . . $0{\cdot}045$

If the molecules are more complicated, it becomes more difficult to determine the value of ρ for each of the secondary radiations corresponding to each intramolecular vibration. The value appears to be able to vary from 0 to $\frac{6}{7}$, according to the importance of the fluctuations in the refractivity of the oscillating molecules in comparison with their fluctuations in anisotropy.

In reality experiments give values which seem to reach unity. On the other hand, $\frac{6}{7} = 0{\cdot}857$, which is very close to 1, and it would be

desirable to repeat the measurements in the case of the large depolarisations, to make certain that the results are actually in excess of $\frac{6}{7}$.

8. Experimental Study of the Depolarisation of Light in Crystals.

To explain the Raman effect in liquids, it appears necessary to assume that light has not the same action on all the molecules; most of them diffuse the light without change of wave-length; a certain number (molecules 1) diminish the frequency by n_1; others (molecules 2), by n_2. Each of these groups of molecules is defined, not only by the corresponding diminution in frequency, but also by the depolarisation of the light which it diffuses. It has been supposed, therefore, that the probable orientation of the molecules of each group varies from one group to another or, in other words, that the action of light on a molecule depends on its orientation. It was therefore of interest to study crystals, where the molecules are oriented in a known small number of directions, by varying the incidence of the primary beam on the crystal.

The first researches were made on quartz and Iceland spar. The image of the horizontal primary beam was projected on to the vertical slit of a glass spectrograph; a Wollaston prism, placed between the collimating lens and the prism, formed a double spectrum, and separated the vibration of intensity i, parallel to the primary beam, from the vibration of intensity I perpendicular to this beam. If careful measurements are made, it is possible to study fairly small crystals (one to two cubic centimetres); I was forced to do this, because all the large crystals of Iceland spar in the laboratory were characterised by troublesome fluorescence, and I could only find a small specimen of Iceland spar perfectly homogeneous and without fluorescence: this was a 30° prism cut, as shown in Fig. 1.

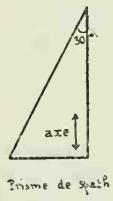


FIG. 1.

When operating on such small specimens, it is difficult to avoid parasitic light, even by immersing the crystal in a vessel containing liquid of nearly the same refractive index. However, the radiations diffused without change of wave-length are alone affected by the parasitic light, and the study of the secondary radiations is not compromised. As regards quartz, this difficulty did not arise, since I had some very pure specimens of large size.

Before proceeding to the study of the state of polarisation of the secondary radiations, I had commenced operations by measuring with precision their wave-lengths on the spectrograms obtained by Daure with his spectroscope, an instrument of great luminosity and dispersive power. The results obtained are given in Tables IV. and V.

TABLE IV.—DIFFUSION SPECTRUM OF QUARTZ.

(Negative radiations in mm.$^{-1}$)

− 12·35	− 20·75 band 4Å	− 26·70	− 35·65	− 40·25 band 4Å	**− 46·70** line 1·5Å
− 70·0	− 79·6	− 106·2	− 116·5	− 128·7	

TABLE V.—DIFFUSION SPECTRUM OF ICELAND SPAR.

+ 27·97	+ 15·39	**− 15·67**	− 22·13	− 28·32 band 3·5 Å	− 71·31
− 108·26	− 143·25	− 175·0			

The most important lines are printed in heavier type. Plate A represents the diffusion spectra of quartz, Iceland spar, and sodium chlorate, obtained with Daure's spectroscope.

With Daure's spectrograph and a Foucault prism *of large aperture placed before the slit*, Daure and I also obtained the spectra of Iceland spar represented on Plate B. The Foucault prism is inconvenient in that it requires two settings (one for the vibration i, the other for the vibration I); a Wollaston prism, on the contrary, gives the two spectra at the same time, which eliminates all error due to variation in the emission of the source of light. However, this plate will give the reader an idea of the beautiful phenomenon of the polarisation of the secondary radiations in crystals, and will illustrate the unexpected results which I have obtained.

The first photograph (1) gives the diffusion spectrum of Iceland spar, the axis of the crystal being parallel to the primary ray Ox. There is no polariser in the diffused beam. Underneath is the spectrum of the iron arc, which was used for the exact measurement of the wave-lengths. We can recognise quite easily in the spectrum of Iceland spar all the radiations mentioned above.

The second photograph (2) gives the two diffusion spectra of Iceland spar photographed through a Foucault prism, with the principal section parallel to the primary ray (i), then perpendicular to this ray (I). The axis of the crystal is always parallel to the primary ray Ox.

The third photograph (3) gives the two diffusion spectra, i and I, in the case where the axis of the crystal is directed along Oz, perpendicular to the plane xOy of the two incident and diffused rays.

9. General Results.

A rapid inspection of these spectra leads at once to remarkable conclusions:

(1) *The lines of spectrum* (1) *are not all in the same state of polarisation.* In photograph (2) they are seen to be distributed between the spectra i and I. The strong line — 108 is almost completely polarised along Oz $\left(\rho = \frac{i}{I} = 0\right)$; the strong lines — 16 and — 28 are polarised at 90° to the preceding; the lines — 71 and — 143 are completely depolarised.

(2) *The state of polarisation of the positive lines is identical with that of the negative lines.* This identity is very clearly seen in spectra 2 and 3 with the lines ± 16 and ± 28.

These two first laws were already known, from the study of liquids, to be true; the anisotropy of the crystal does not yet function, but only the individual anisotropy of molecules oriented at random.

(3) *The intensity and the depolarisation of the secondary radiations of a crystal depend on the orientation of the crystal.* This experimental fact proves that the orientation of the virtual oscillators, which emit the different secondary radiations, is associated with that of the crystal, and that the probability of excitation by the incident radiation depends on this orientation.

Thus, the lines ± 16 and ± 28 have a depolarisation of about 3·6 when the axis of the crystal is parallel to Ox, and of about 1·5 when this ternary axis is parallel to Oz. The lines — 71 and — 143 are completely depolarised in the first case, and completely polarised ($\rho = \infty$) in the

second case. The line — 108 is nearly completely polarised in both cases ($\rho = 0$), but its intensity changes from 4 to 1.

(4) *There are strong secondary radiations in crystals whose depolarisation is greater than unity*, whilst, in liquids, ρ was found to be always less than unity. In Iceland spar, all the secondary lines, except 108, have a depolarisation greater than unity.

At first sight, this last result does not appear surprising. If the oscillators have fixed axes of oscillation in the crystal, and if the orientation of the crystal is such that these axes are nearly in the direction of the incident ray *Ox*, the depolarisation should have a very high value. Let us suppose, for instance (Fig. 2), that the oscillations can only occur in the direction *Ov* of the plane *xOz*, which makes the small angle α with *Ox*. Let *Z* be the incident electric vector. The force acting is the projection $Z \sin \alpha$ of *Z* on *Ov* and the intensities of the two vibrations, *i* and *I*, are proportional to $(Z \sin \alpha \cos \alpha)^2$ and $(Z \sin^2 \alpha)^2$. Whence $\rho = \cot^2 \alpha$, a very high value. But in this case each of the vibrations *i* and *I* has a feeble intensity, since *Z* is almost normal to *Ov*. The corresponding secondary radiation ought to be much weaker than the radiations for which the depolarisation borders on zero. Now, this is not the case: the line — 28 is at least as intense as the line — 108.

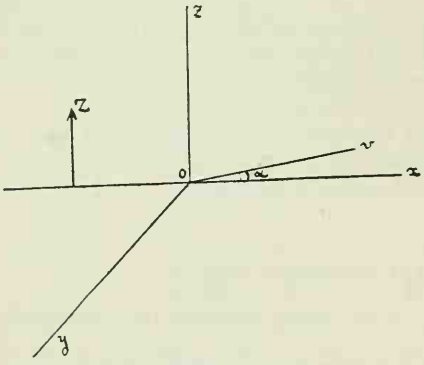


FIG. 2.

On the other hand, if we turn the axis of the crystal by 90° around the diffused ray *Oy*, it would seem that the depolarisation, originally greater than one, should assume a value less than 1, at the same time that the intensity of the secondary radiation in question should increase considerably. Now, this is not the case: when one passes from photograph 2 to photograph 3, the depolarisation of the line — 28 varies only from 3·6 to 1·5, and the total intensity $I + i$ does not change.

(5) *We must, therefore, renounce the theories previously outlined to explain the depolarisation of secondary radiations in liquids.* The connection between the exciting vibration and the virtual oscillator which characterises the state of polarisation of the diffused vibration, is not as direct as was thought. A vibration parallel to *Oz* can excite an oscillator in the perpendicular plane *xOy*. *The oscillator which emits a secondary radiation can vibrate normally to the incident electric force.* This result follows immediately from a consideration of photograph 3, where the lines 71 and 143 are completely polarised along *Ox*, at 90° to the exciting wave.

It will be seen from these few remarks that important conclusions can be drawn from a thorough study of the diffusion spectra of crystals. An unexpected light is thrown on the reciprocal reactions of matter and radiation, and the investigation will, no doubt, enable us to penetrate deeply into the analysis of crystalline structures.

10. Investigations on Iceland Spar.

The crystal of Iceland spar was illuminated first of all by natural light, then by light polarised along either *Oy* or *Oz*; the axis of the crystal was directed along *Ox* (incident ray), then along *Oy* (diffused ray), then along *Oz*. It is convenient, for interpretation of the results, to consider each secondary radiation as emitted by *virtual oscillators*. This system of oscillators has the elements of symmetry of the crystal, and the mean square of the electric displacement along each of the three axes *Oxyz* can be calculated for this system of oscillators by means of the nine negatives obtained.

I have studied in this way the two principal secondary radiations of Iceland spar.

(*a*) *Lines* $\pm$ 28 *mm.*$^{-1}$.—An incident *extraordinary* vibration does not produce a displacement along the ternary axis; it gives the same mean square *a* along any direction of the plane normal to the axis. An *ordinary* vibration gives the mean square *c* along the axis, and *b* along *any* direction on the normal plane. I obtained $a = 4{\cdot}6 \times b$ and $c = 3{\cdot}6 \times b$.

It is seen that, to obtain a displacement along the ternary axis, it is necessary to have an exciting vibration perpendicular to this axis. The displacement of the oscillator is normal to the exciting vibration. On the other hand, the intensity *b* is the same in the direction of the exciting vibration as in the perpendicular direction, instead of being three times as great in the first case. Fig. 3 tabulates these results.

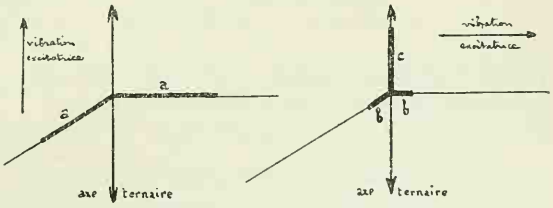


Fig. 3.

The lines $\pm$ 16 and $\pm$ 22 appear to have, in each case, the same depolarisation as the radiation just considered, and to behave in a similar manner. They have, probably, a common origin, and belong to the same group.

(*b*) *Line* — 108 *mm.*$^{-1}$.—The displacement of the system of oscillators which diffuses this radiation is always parallel to the incident vibration, whether this be *parallel* or *perpendicular* to the ternary axis. From this it follows that the depolarisation is zero in the nine negatives. The mean square of the displacement is four times as large in the second case as in the first.

This line is therefore emitted, either by oscillators agreeing in phase, which have, as a whole, the symmetry of the crystal, or rather, as we shall see, by oscillators without definite phase relationship, each of which, according to this second hypothesis, possesses the symmetry of the crystal.

The frequency $n = 108{\cdot}26$ mm.$^{-1}$ is, as a matter of fact, the inverse of the wave-length 9·23 μ. It is, therefore, the *inactive* oscillation of Kornfeld's theory of infra-red spectra, which has no corresponding absorption band, but whose frequency occurs in the combination formulæ from which infra-red absorption bands are derived. Schäfer and his collaborators have attributed it to the ion CO_3. Leontowitsch has found it in aqueous solutions of potassium carbonate ($\lambda = 9{\cdot}26$ μ), from which the secondary radiation 28 mm.$^{-1}$ had disappeared. The group

of radiations 16, 22, 28 has its origin, therefore, in the oscillations of the crystalline system, whilst the radiation 108 is due to oscillations within the ion CO_3.

The line 108 of Iceland spar is polarised in the same direction as that of the exciting vibration, whether this last be parallel or perpendicular to the axis of the crystal. It follows from this that the ion CO_3 has its three oxygens in a plane normal to the axis; analysis of the crystalline structure by means of X-rays had already given the same result. On the other hand, the fact of finding the same line 108 of the ion CO_3, both in the crystal of Iceland spar, and in a solution of potassium carbonate, shows that the ion already possesses its own individuality in the crystal, that is to say, that the oxygens are much more intimately attached to the carbon atoms than to the Ca^{++} ions.

FIG. 4.

Let us consider one of the CO_3 ions (Fig. 4). When the exciting luminous vibration is perpendicular to the plane of the atomic nuclei, the linear oscillator which emits the radiation 108 has an amplitude twice as weak as in the case where the exciting vibration is parallel to the plane of the atoms. By introducing the coefficients of anisotropy A, B, C, which are well known in the classical theory of molecular diffusion,[6] we get :—

$$A = 1, \qquad B = C = 2, \qquad x = \frac{A}{B} = \frac{1}{2}.$$

Whence the depolarisation of the light diffused by CO_3 ions distributed at random, that is to say, in solution, is :—

$$\rho = \frac{2(x-1)^2}{4x^2 + 2x + 9} = \frac{1}{22} = 0{\cdot}045$$

It would be interesting to verify this result directly.

(*c*) *Line* — 71 *mm.*$^{-1}$.—This line appears to be completely depolarised (incident light natural) when the ternary axis of the Iceland spar is parallel to the incident ray Ox; it is almost completely polarised (ρ very large) when the ternary axis is parallel to Oz. The weak line — 143 behaves exactly like the preceding one; these two radiations must, therefore, be grouped together. It is remarkable that one of the frequencies is almost exactly twice the other: $71{\cdot}31 \times 2 = 142{\cdot}62$ (instead of 143·25). This appears to be the first time that a harmonic has been definitely found in a Raman spectrum.

11. Investigations on Quartz.

Quartz has only been studied in natural incident light.

(*a*) *The axis of the crystal being normal to the two incident and diffused rays*, the lines $\pm$ 46·7 and $\pm$ 20·7 mm.$^{-1}$ are almost completely polarised along Oz $\left(\rho = \frac{i}{I} \leq 0{\cdot}05\right)$, whilst *the lines* — 26·7 *and* — 79·6 *appear to be completely polarised at* 90° *to the former ones* (ρ considerably greater than 1). As we have already had occasion to remark, this last result is not quite inexplicable; linear oscillators ought to give a vibration i greater than I if they are sensibly parallel to Ox.

(*b*) *If, however, the axis of the quartz is made to coincide* with Ox, a permutation of the intensities I and i would be expected; or, rather,

it would be expected that a depolarisation greater than unity should become less than unity: now, *the state of polarisation of the secondary radiations just quoted does not change to an appreciable degree.*

The lines ± 13 appear to behave differently: they appear to be greatly polarised (ρ very large) in the case (a) and to be completely depolarised ($\rho = 1$) in case (b). Unfortunately, the ray diffused without change of wave-length is so intense that it interferes with the study of the neighbouring line ± 13 in the case of the spectroscope with small dispersive power which we have been using.

In a general manner, it may be said that the study of quartz, with which we started, is actually less advanced than that of Iceland spar. New measurements must be made with a spectrograph which is more luminous, and which has a higher dispersive power. We are having a spectrograph constructed for this purpose, a slightly modified instrument of the Daure type.

A STUDY OF THE "RAMAN EFFECT" IN SOME LIQUEFIED GASES.

By Professor P. Daure (Montpellier).

Received 29th May, 1929.

The "Raman Effect" is a secondary effect of molecular scattering of light by material media, scattering sometimes named "The Tyndall phenomenon."

A material medium lighted by a monochromatic radiation of wave-number N_0, becomes the seat of a luminous radiation composed:

(1)—of the incident radiation N_0 (molecular scattering of light, Tyndall phenomenon);

(2)—of secondary radiations of smaller intensity, characteristic of the studied medium, and which constitute the "Raman Effect."

The wave-numbers of those secondary radiations are:

$$N_0 \pm n_1,\ N_0 \pm n_2,\ N_0 \pm n_3 \ldots N_0 \pm n_j.$$

The n_1, n_2, n_3 . . . n_j quantities are independent of N_0. They differ considerably according to the molecular constitution of the medium. We will call them "*characteristic frequencies of the medium*," and render them in wave-numbers to the millimetre.

Experiment and theory have proved that[1] the negative secondary lines $N_0 - n_j$, situated towards the red, are always more intense than the corresponding positive lines $N_0 + n_j$.

The negative lines then allow the more ready determination of the characteristic frequencies; for that reason, in the following pages *we shall only concern ourselves with the negative lines*, which alone have been the object of our study.

n_j characteristic frequencies are, on the other hand, frequencies of molecular absorption, corresponding most frequently to frequencies determined by the study of the infra-red absorption.

[1] Raman and Krishnan, *Ind. Journ. Physics*, **2** (1928), 399; Cabannes, *C.R.*, **186**, (1928), 1714.

These essential properties of the Raman Effect were rapidly established; it became then interesting to look for the characteristic frequencies of substances of simple molecular structure. Having first studied in their liquid state the chlorides of the elements in columns 5 and 6 of the periodical classification,[2] I then sought to determine the Raman spectrum of more simple molecules HCl, NH_3, CH_4 . . ., which I examined in their liquid state and at atmospheric pressure.

Experimental Methods.

To study the Raman Effect produced by a transparent object, we must analyse by the spectrograph the light it emits when illuminated by a light either monochromatic or made up of a small number of monochromatic radiations. Liquids are easily placed into a cylindrical horizontal tube, on the axis of which is projected, laterally, the image of a mercury vapour lamp; the light emitted along the axis of the tube, perpendicular to the mean direction of the incident cone, is then observed.

This method has also been used in the case of liquefied gases, by using a tube small enough to be contained in a Dewar flask. The tube containing the liquefied gas (6 cm. in length, 1 cm. in diameter), was placed horizontally in a non-silvered Dewar flask of Pyrex.

The refrigerants used were: in the study of methane liquid, commercial liquid oxygen; in every other case alcohol cooled to a convenient degree by a tube also placed in the Dewar flask, and into which was thrown liquid oxygen or carbonic snow.

I projected on the axis of the tube the light from a quartz mercury vapour lamp (Gallois type, see-saw system), kept in the horizontal position, after lighting. The light thrown out along the axis was condensed on the slit of the spectrograph.

This spectrograph had been constructed before the discovery of the Raman Effect, for the study of sources of feeble intensity. It is made of two prisms of flint, 5 cm. high, 10 cm. long, cut by MM. Jobin and Yvon.

The photographic object-glass was made by the "Société Générale d'Optique" (formerly Etablissements Huet) according to the calculations of M. Cojan, the optician of that Society, and consisted of two achromatic lenses, thus making it possible to obtain a numerical aperture of $f/1{\cdot}8$.

The first lens can be used alone, when the numerical aperture is $f/3$.

With this lens alone I have carried out all my spectrograms of the Raman Effect, so as to have a larger separation of the lines.

The linear separation thus obtained is

20 Å.	for 1 mm.	towards	4100 Å.
32 Å.	,,	,,	4400 Å.
55 Å.	,,	,,	4900 Å.

The mechanical features of the spectrograph were carried out by M. Bouty, engineer in Paris.[3]

A Study of the Negatives.—The Raman spectra obtained were measured in terms of the spectra of the iron arc. The spectral interval actually used as a means of measurement extended from 4050 Å. to 5100 Å. This

[2] Daure, *C.R.*, 187 (1928), 940.

[3] This spectrograph has been described in the *Revue d'Optique théorique et instrumentale*, 7 (1928), 450-456.

interval contains a very few feeble mercury lines which might be mistaken for Raman lines, but they can readily be distinguished.

The exciting lines of the Raman lines observed were sometimes the group 3650 Å.; most frequently, however, the two strong lines 4046 Å., 4358 Å.

In order to determine without ambiguity the exciting radiation of each observed line, I compared a negative of the exciting lines aforementioned with a negative obtained with the 4358 Å. line alone, which was easily isolated by placing in the path of the incident cone a tube of acid sulphate of quinine.

The wave-length of a Raman line being determined, and that of its exciting line known, a subtraction of wave-numbers gives the characteristic frequency. The only Raman lines observed being negative ones, we can write:

$$n_j = N - N_j.$$

Experimental Results.

The following table gives, *in wave-numbers to a millimetre*, the characteristic frequencies of the liquefied gases studied. In most cases the lines obtained were very clear, although in the hydrochloric acid and ammonia there could be seen bands of some Å. The characteristic frequency given corresponds to the maximum intensity of the band.

S., m., f. stand for relative intensities: strong, medium, feeble.

	k.		*l.*	*h.*			
HCl	—	—	—	—	278	—	—
NH_3	107 f.	—	158 f.	321 S.	330 S.	338 S.	—
CH_4	—	—	—	—	290·8	—	—
C_2H_6	99 m.	—	146 m.	289 S.	—	295 S.	—
C_3H_8	87 m.	94 f. 165 f.	145 m.	287 S.	291 S.	295 S.	—
C_2H_4	134 m.	—	162 m.	—	—	300	308 m.
C_2H_2 dissolved in acetone	[4]	—	196 S.	—	—	—	332 f.

It is interesting to compare the characteristic frequencies obtained with those recently given by Mr. Wood [5] on HCl and NH_3 gases. From his results it can easily be inferred that HCl gaseous gives one line of characteristic frequency 288·7 wave-numbers to a mm. Gaseous NH_3 gives one line of 331.

It is seen in the first place that gaseous and liquid hydrochloric acid give clearly different spectra, though it is impossible to explain the anomaly.

[4] The corresponding line has not been observed, it may have been covered up by a line of the solvent, acetone.

[5] *Phil. Mag.*, 7 (1929), 744.

Then, it is to be noted that the line observed by Mr. Wood in ammonia gas corresponds to a central band, wave-number 330, observed in the liquid. The complexity of the spectrum of the liquid, which is analogous to that of ethane, would prove that gaseous ammonia is formed with molecules NH_3, and liquid ammonia with molecules $H_3N = NH_3$.

Interpretation of the Results.

It is not yet possible to give a complete interpretation of Raman spectra of substances of known molecular constitution, but one can, at any rate, make the following remarks :—

H *lines.*—Hydrogen compounds give lines of high characteristic frequencies, going from 278 to 340 wave-lengths to the mm. Those lines are attributable to the linkage of a metalloid (M) with hydrogen (H). (This remark has already been made by most of those who have studied the Raman Effect.) We will call them H *lines.*

Moreover, the results obtained upon liquid methane and liquid hydrochloric acid (Mr. Wood's results on gases) show that those are the only lines due to the M-H combination.

Other lines.—Lines of lower characteristic frequencies (wave-number from 0 to 196), which can be noticed particularly in C^2 hydrocarbons are attributable to interior linkage of M-M. In the most complex hydrocarbon chains, these lines are sometimes very numerous. In the simplest hydrocarbon chains (ethane, ethylene) those lines are two in number, *k* and *l*, although it is impossible to say what they mean.

The position of the *l* lines depends, in organic compounds, on the nature of the carbon linkage :—

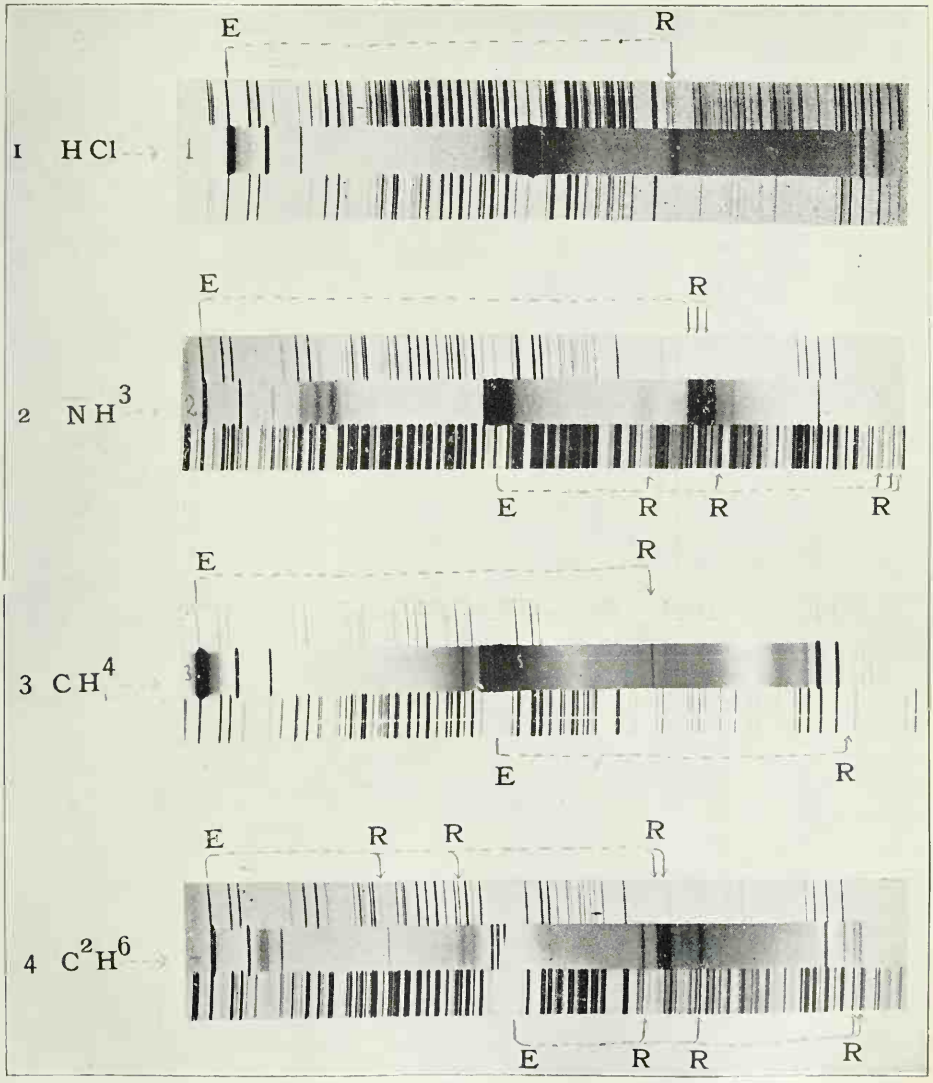
Organic compounds with a simple linkage (ether, alcohol) show an *l* line in the neighbourhood of wave-number 145 (from 143 to 146) as in the case of ethane.

Organic compounds with a double linkage between carbon atoms (benzene and its derivatives) show an *l* line, in the neighbourhood of wave-number 160 (from 158 to 162) as in the case of ethylene.[6]

Lastly, the only acetylenic hydrocarbon studied, acetylene, has a line *l* of wave-number 196.

These few remarks may be of some interest in the study of the molecular constitution of hydrogen compounds, but it is impossible, for the time being, to find a basis for a general interpretation of the Raman spectra by means of their chemical formula; for the chlorides of the $C Cl_4$ type, which have a constitution not unlike that of methane, have a much more complex spectrum, formed by four lines of nearly equal intensity.

[6] Organic compounds having the C = O linkage give also a line of frequency in the neighbourhood of 170 wave-lengths to the mm.

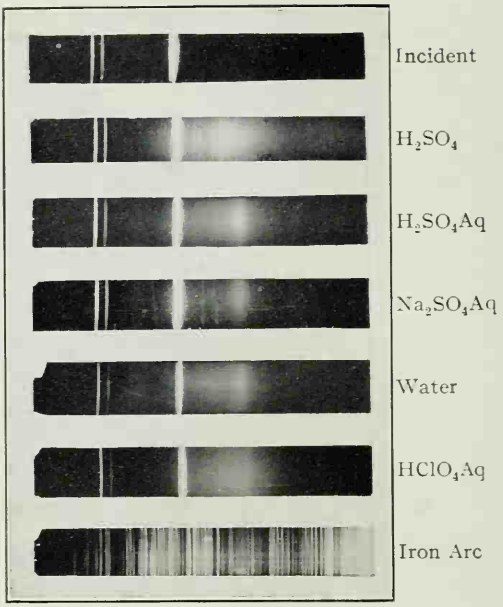


This plate shows the original photographs enlarged three times. Each Raman spectrum is compared with two iron spectra. The most visible Raman lines are indicated by the letter R; the exciting mercury lines, by the letter E.

It should be noted that the exciting radiation 4358 Å was screened off, in order to reduce the fogging in the Raman spectrum of C_2H_6.

[*Daure.*]

[*To face page* 828.



[*Taylor—The Raman Effect of AX_4 groups.* *See page* 830.]

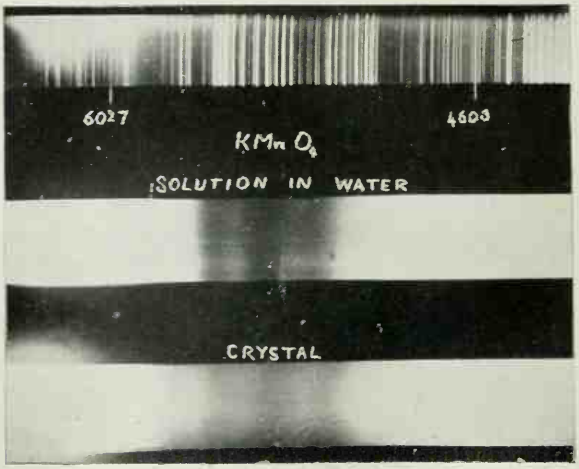


FIG. 1.

[*Taylor—Band Spectrum of $KMnO_4$.* *See page* 860.]

[*To face page* 829.

RAMAN LINES IN THE SPECTRUM OF THE ELECTRIC DISCHARGE.

By Professor H. S. Allen, University of St. Andrews.

Received 18th July, 1929.

In a letter which appeared in *Nature* of 26th January, it was suggested that many faint lines in the secondary spectrum of hydrogen arise from Raman light-scattering. When hydrogen gas is subjected to an electric discharge the lines of the Balmer series are emitted by atoms of hydrogen, and the neighbouring molecules of gas must be subjected to bombardment by light quanta of corresponding frequency. Hence, we should expect each Balmer line to be accompanied by a system of fainter lines which may be termed the Raman companions. In the same way some, at least, of the stronger lines in the secondary spectrum of hydrogen might be accompanied by Raman companions. In the experiments of Raman on liquids, lines having enhanced frequency are present, but the intensity of such lines is less than the intensity of lines having diminished frequency. The conditions in a discharge tube are quite different from those in a liquid exposed to an external source of light, for in consequence of collisions excited molecules must be present in considerable numbers. Consequently, it may conceivably happen that a Raman line on the violet side of an exciting line may be just as intense, or even more intense, than the corresponding Raman line having diminished frequency.

Among the factors which determine the intensity of a particular Raman line are (1) the intensity of the exciting line which, in turn, depends upon the number of atoms or molecules acting as emitter for that particular line; (2) the relative abundance of molecules present in a state appropriate to the particular emission concerned. These factors are likely to be extremely complicated, depending as they do on the conditions of the discharge tube in the particular region which is employed in the experiments. For example, in R. W. Wood's discharge tube which gave the Balmer lines strongly there are probably many atoms, but comparatively few molecules. The way in which the intensity of a Raman line depends upon the frequency of the exciting light has been discussed by Hill and Kemble and others.

In considering the possibility of recording Raman companions photographically, one must take into account the sensitiveness of the plate or film for the particular region under investigation, and also the effect of any continuous spectrum which may be present in masking very faint lines.

In *Nature*, 4th May, page 694, Dr. D. B. Deodhar has drawn attention to the results which he has obtained in support of the view put forward by the writer by using the wave-length tables of Finkelnburg. The number of lines now known in the secondary spectrum of hydrogen is so large that great care is required to make sure that agreement is not merely the result of chance, but investigations which are still in progress confirm the hypothesis that Raman companions are actually present in that spectrum.

In a private communication Professor O. W. Richardson has kindly drawn attention to the fact that several of the lines referred to in *Nature* of 26th January belong to the band systems which he has been investigating, and he has also emphasised the high degree of accuracy which is found for those systems.

With the assistance of Dr. Sandeman a systematic examination of the hydrogen spectrum for Raman companions is now being made.

The University,
St. Andrews.

THE RAMAN EFFECT OF SOME AX_4 GROUPS.

By A. M. Taylor, *Professor of Physical Optics in the University of Rochester, N.Y.*

Received, 26th August, 1929.

In the early stages of the brief history of the Raman effect, it was considered that a Raman line was separated from the parent line by a frequency difference equal to a frequency of vibration of the molecule in the infra-red. This simple theory is now superseded, it being implicit in the Kramers-Heisenberg theory of dispersion that a Raman frequency difference is one corresponding to an otherwise forbidden transition between two allowed states of the molecule. As an example of this, the Raman lines from HCl gas[1] may be quoted, where the forbidden Q branch is found. It therefore has now become a matter for explanation when the Raman lines do correspond with an infra-red frequency, in contrast to earlier ideas when it was the deviations from infra-red values that had to be explained.

While the theory of the Raman effect was still in its earlier stage, it was thought to be advantageous to examine the scattering from AX_4 groups in various solutions, in order to determine the frequencies of internal oscillation of the groups under the conditions existing in the liquid phase. Alkali sulphates, pure sulphuric acid, and strong aqueous perchloric acid were all found to give modified lines in the scattered spectrum. The solution of the sulphates and dilute sulphuric acid in water gave very weak lines, whereas the pure anhydrous acid and also strong perchloric acid gave very beautiful sharp lines.

Experimental.

The experimental arrangement was of the simplest. The only spectroscope available was a small Hilger constant deviation instrument, with lenses of 31·5 mm. aperture and 285 mm. focal length; the light gathering power was therefore small. The eyepiece was replaced by an old bellows camera with lens removed, the back of which racked for focussing. The light from an automatic quartz-mercury lamp running at atmospheric pressure was focussed by an 8-inch condenser on to a $1\frac{1}{2}$-litre flask of non-fluorescent glass. This contained the liquid under examination, and light scattered at right angles to the beam entered

[1] R. W. Wood, *Phil. Mag.*, **7**, 744, 1929.

the slit of the spectroscope directly. The slit was shielded from any illumination by the direct beam by a black velvet hood. A filter of cobalt glass inserted in the path of the direct beam allowed only the blue and violet light to pass from the mercury arc. The intensity of the modified lines in the spectrum of the scattered light was exceedingly small, but by giving four or five days' exposure, photographs could be obtained. The lamp being self-lighting, it could be left running off the 200 volt mains without attention, for weeks on end. The plates used were Ilford Special Panchromatic, Speed H and D 2000. The lines were measured up on a microscope with travelling stage, and were assigned their correct wave-length by comparison with a photograph taken of an iron arc, the spectroscope being untouched during the interval between the photographing of the Raman and comparison spectra.

Results.

The results are given in Tables I. to IV.

TABLE I. RAMAN LINES FROM PURE H_2SO_4.*

Raman Lines.		Exciting Line.	Wave-number Difference.
Wave-length in Å.	Wave-number in cm.$^{-1}$.		
4139·8	24,156	24,711	555
4171·0	23,970	24,521	551
4204	23,787	24,711	924
4239	23,590	24,711	1121
		24,521	931
4278·4	23,373	24,711	1338
		24,521	1148
4310·8	23,198	24,521	1323
4436·7	22,539	22,943	404
4468·6	22,378	22,943	565
4539·5	22,029	22,943	914
4584·2	21,814	22,943	1129
4624·0	21,626	22,943	1317

Mean values of Raman wave-number differences 404, 557, 923, 1133, and 1326.

TABLE II. RAMAN LINES FROM DILUTE H_2SO_4 AQ.

Raman Lines.		Exciting Line.	Wave-number Difference.
Wave-length in Å.	Wave-number in cm.$^{-1}$.		
4446	22,492	22,943	451
4476	22,341	22,943	602
4555	21,954	22,943	989
4603	21,725	22,943	1218

Wave-length.	Wave-number.
4046·8Å.	24,711 cm.$^{-1}$.
4078·1	24,521
4358·6	22,943

* The exciting lines in the spectrum of incident light were as follows:—

TABLE III. Raman Lines from Aqueous Solutions of Alkali Sulphates.

Raman Lines.		Exciting Line.	Wave-number Difference.
Wave-length in Å.	Wave-number in cm.$^{-1}$.		
4446	22,492	22,943	451
4478	22,330	22,943	613
4555	21,954	22,943	989
4603	21,725	22,943	1,218

TABLE IV. Raman Lines from Strong $HClO_4$. Aq.

Raman Lines.		Exciting Line.	Wave-number Difference.
Wave-length in Å.	Wave-number in cm.$^{-1}$.		
4204·9	23,782	24,711	929
4446	22,491	22,943	452
4478	22,330	22,943	613
4544·1	22,007	22,943	936
4586	21,803	22,943	1140

A few criticisms of the results may be made. The lines from pure sulphuric acid are strong and sharp, and are found to be excited by three different lines in the incident spectrum, *i.e.*, the two strong violet lines 4046·8 Å. and 4078·1 Å., and the strong blue line 4358·6 Å. There is little doubt of the correct ascription of the lines, as the way indicated in the third column of the table is the only one which gives agreement between the various wave-number differences.

Most of the lines given in Tables II., III., and IV. are, as reference to Plate I. will show, very faint and elusive to measure. There is no doubt in the case of the 4205 Å. and 4544 Å. lines from $HClO_4$ which are clear and sharp, and correspond to the same Raman frequency stimulated by two different lines in the incident spectrum. There is, however, a certain doubt concerning the line at about 4477 Å., which occurs in all the scattered spectra, as to whether it is due to the water or to the AX_4 group. Water [2] shows a band at 4480 Å., according to Raman and Krishnan, but this band does not show up, or is at least very faint, in my own photographs of scattering from pure water. I have, therefore, considered that the line measured at approximately 4477 Å. is quite probably genuine, and due to the AX_4 group, particularly as it is needed to represent the fundamental frequency ν_1 of the group.

Discussion of the Results.

The results are collected and compared with other relevant data in Table V. In this table are given, where possible, the frequencies (expressed as wave-numbers) of the maxima of absorption and of reflection in the infra-red. The frequencies in the fourth column are higher than the corresponding frequencies in the third column because of the Forsterling-Havelock [3] correction, which results in maxima of reflection

[2] Raman and Krishnan, *Ind. J. Physics*, **2**, 399, 1928.

[3] Forsterling, *Ann. Physik*, 61, 577, 1920; Havelock, *Proc. Roy. Soc.*, A. 86, 1, 1911; and A. 105, 488, 1924.

occurring at higher frequencies than the corresponding maxima of absorption. The latter are usually considered to coincide with the true frequency of oscillation of the vibrator concerned.

The general correspondence of the Raman frequency differences in the first column of Table V. with the characteristic infra-red frequencies, makes it clear that we are dealing with a case where the Raman lines appear to be accounted for by simple correlation with infra-red spectra.

TABLE V.

Substance.	Raman Wave-number Difference.	Infra-Red Absorption Maximum.	Infra-Red Reflection Maximum.	Suggested Origin.
H_2SO_4 (pure)	404 cm.$^{-1}$ ($24{\cdot}8\mu$)	—	—	$\nu_2 - \nu_1$
	557 ($17{\cdot}9$)	—	—	ν_1
	923 ($10{\cdot}8$)	—	970 cm.$^{-1}$* ($10{\cdot}3\mu$)	ν_2
	1133 ($8{\cdot}8$)	—	1163* ($8{\cdot}6$)	$2\nu_1$
	1317 ($7{\cdot}6$)	—	1390* ($7{\cdot}2$)	$2\nu_2 - \nu_1$
H_2SO_4Aq.	451 ($22{\cdot}2$)	—	—	$\nu_2 - \nu_1$
	602 ($16{\cdot}6$)	—	—	ν_1
	989 ($10{\cdot}1$)	—	1040* ($9{\cdot}6$)	ν_2
	1218 ($8{\cdot}2$)	—	1163* ($8{\cdot}6$)	$2\nu_1$
SO_4 - - Aq.	450 ($22{\cdot}3$)	—	—	$\nu_2 - \nu_1$
	614 ($16{\cdot}3$)	—	625† ($16{\cdot}0$)	ν_1
	989 ($10{\cdot}1$)	1096‡ ($9{\cdot}12$)	1111† ($9{\cdot}0$)	ν_2
	1218 ($8{\cdot}2$)	1360‡ ($7{\cdot}35$)	—	$2\nu_1$
$HClO_4$Aq	453 ($22{\cdot}1$)	—	—	$\nu_2 - \nu_1$
	614 ($16{\cdot}3$)	—	—	ν_1
	937 ($10{\cdot}6$)	—	—	ν_2
	1140 ($8{\cdot}7$)	—	—	$2\nu_1$
$KClO_4$ cryst.	—	720‡ ($13{\cdot}9$)	—	ν_1
	—	1080‡ ($9{\cdot}25$)	—	ν_2
	—	1430‡ ($7{\cdot}0$)	—	$2\nu_1$

* Pfund's [4] measurements with the liquid.
† Schaefer and Schubert,[5] measurements with anhydrous crystals.
‡ A. M. Taylor's [6] measurements with anhydrous crystals.
[4] Pfund, *Astrophys. J.*, **24**, 19, 1906.
[5] Schaefer and Schubert, *Ann. Physik*, **50**, 283, 1916.
[6] A. M. Taylor, see paper contributed to this discussion, p. 860.

The Energy Diagram of the AX_4 Group.

The fifth column of Table V. contains suggestions as to how the observed frequencies arise, whether in the infra-red or in the Raman spectra. Rolan [7] showed that the AX_4 group has two fundamental vibrations; in this it presents similarities to methane CH_4, a similarly constituted group; two frequencies, ν_1 and ν_2, are therefore chosen to explain the spectrum. The other three frequencies generally observed then fall in fairly well, as due to $\nu_2 - \nu_1$, $2\nu_1$ and $2\nu_2 - \nu_1$. The energy levels of the AX_4 group are sketched in Fig. 1. Raman frequencies correspond to transitions between two states, ν_1 and any other level. Thus, the absence of $\nu_1 + \nu_2$ is accounted for. On the right of the diagram are indicated the transitions which give rise to the major infra-red absorptions. The quantum numbers may change by more than one unit because of the anharmonic nature of the forces within the AX_4 group.

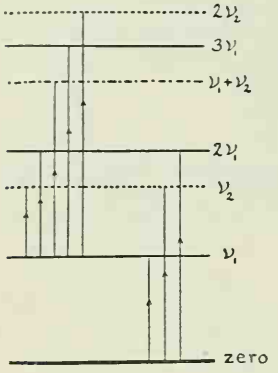


FIG. 1.

Loosening of Constraints within the AX_4 Group.

The Raman frequencies, therefore, are supposed to correspond with the infra-red frequencies as the energy diagram shows; nevertheless, there are striking differences apparent if Table V. be studied. Apart from the Forsterling-Havelock difference between figures in the third and fourth columns, it will be seen that figures representing frequencies of internal vibration of the AX_4 group in the liquid state are much smaller than those representing corresponding oscillations in the solid state. This is similar to the effect observed in the band spectrum of $KMnO_4$ in the visible region,[8] where the frequency of internal vibration of the MnO_4 ion is less in aqueous solution than it is in the crystalline lattice. From Table V., however, it is clear that not only is the frequency of vibration less in the hydrated SO_4^{--} ion than it is in the same ion in the crystal lattice, but that the frequency is still smaller in pure sulphuric acid. This is true if we compare values found only in the infra-red, or if we include the Raman values. Unfortunately, these latter do not exactly coincide with the Pfund values, and there is no indication whether this is to be attributed to some deviation of the position of the Raman lines from that indicated by the theory, or whether Pfund's values are inaccurate. His measurements are only rough and too much weight must not be given to them.

The Location of the H^+ Ions.

It is, nevertheless, illuminating to compare the values, however obtained, for the frequencies of vibration of the SO_4 group in pure sulphuric acid and in aqueous solutions. It appears that, if the sulphate ion be removed from the crystal lattice and hydrated, the frequency of

[7] Rolan, *Z. Physik*, 39, 588, 1926.
[8] A. M. Taylor, see paper contributed to this discussion, p. 860.

internal oscillation is lowered; if the water be removed and two H_+ ions substituted the frequency is lowered still more. The effect of the two hydrogen ions is greater than the effect of the atmosphere of oriented polar water molecules which surround an SO_4 ion on hydration; the positive metallic ions in a crystalline lattice of the sulphate have a smaller influence upon the group than either. This sheds an interesting light upon the location of the H^+ ions in sulphuric acid. The hydrogen ions can only exert this strong influence if they have approached very close to the group. They are too small to remain at any great distance, and they have most probably dived down beneath the outer electronic shell.

It is not in the least surprising to find that the H^+ ions have penetrated the SO_4^{--} group, and that they are most likely to be buried within it, but it is delightful to observe this to be indicated by the Raman lines, being made evident by the slowing down of the internal vibrations of the group. The hydrogen ion is known to have almost lost its identity in the hydrogen halides, so much so that the halides crystallise in molecular lattices. The SO_4^{--} ion, with its extremely symmetrical constitution, presents some analogies to the halogen ion, *e.g.*, both have a large deformability, and it is suggested that crystalline sulphuric acid must similarly have a molecular lattice. The fact that K_2SO_4 melts at 1070° C., whereas H_2SO_4 melts at 10·5° C., indicates the great dissimilarity between their crystalline lattices.

Summary.

The Raman spectra of H_2SO_4, $HClO_4$, and of the alkali sulphates in solution has been photographed, measured, and compared with infra-red spectra. The energy diagram of the AX_4 group is indicated. The frequency of vibration of the AX_4 is found to be diminished on destruction of the crystal lattice and hydration of the group, and in the case of SO_4^{--} to be still further diminished by the removal of the water and addition of H^+ ions to form molecular H_2SO_4. It is inferred that the hydrogen ions have penetrated the SO_4 ion, and it is suggested that H_2SO_4 must crystallise with a molecular lattice.

It is with great pleasure that I thank Professor T. M. Lowry, F.R.S., in whose laboratory I have worked, and the Ramsay Memorial Fellowship Trustees under whose auspices this work has been achieved.

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A NOTE ON THE PLANE-POLARISATION OF THE RAMAN SPECTRA AND ON RAMAN LINES SCATTERED FROM COARSELY POWDERED CRYSTALS.

By A. C. Menzies, M.A., D.Sc.

Received, 15th July, 1929.

Plane-Polarisation.

It has been observed by Raman and many other investigators that in Raman spectra many of the lines are plane-polarised in a direction parallel to that of the unmodified lines, while the other lines are unpolarised.

No explanation of this has as yet been put forward which accords with the Kramers-Heisenburg dispersion theory, which accounts so well for the Raman shifts caused by gases (*viz.*, that the Raman lines are caused by transitions between energy levels having a third common level).

The writer has made experiments on the polarisation of the lines in the spectra of the light scattered by liquids (*e.g.*, CCl_4) in a direction perpendicular to the incident beam and in a direction obliquely forward (about 160°). Also experiments have been made on the polarisation of lines in the spectra of the light scattered by crystalline quartz placed with the optic axis perpendicular to the incident and scattered beams, and with the optic axis parallel to the incident beam.[1]

It is concluded that many of the facts could be accounted for by considering the initial and final directions of vibration in the molecule involved to be parallel in the case of the polarised lines, perpendicular in that of the unpolarised lines, and at an oblique angle in the case of partially polarised lines.[2]

The Production of Raman Lines by Scattering from Coarsely Powdered Crystals.[3]

So far, experiments on scattering of light by solids have had to be restricted to such substances as could be obtained in large transparent specimens.

Desiring to compare the fundamental frequencies of vibration of some soluble crystals in the solid state with those of the same substances in solution, it was necessary to be able to determine the frequencies of solids not usually obtainable in large clear specimens. It occurred to the writer that it might be possible to obtain Raman lines by reflecting light off crystal surfaces. Accordingly an attempt was made with

[1] These latter experiments were anticipated by Cabannes, *Comptes Rendus*, vol. 188, p. 249, 1929. The writer's results are in agreement with those of Cabannes, but are fuller.

[2] A fuller account of this work will appear shortly in the *Philosophical Magazine*, but it was thought desirable to bring it before this conference for discussion.

[3] Contributed verbally on 25th Sept.

potassium nitrate; a flask was filled with the coarsely-powdered crystals, and light from a quartz mercury-vapour lamp was directed on the crystals, and observation made with a Hilger constant deviation spectrograph of small light-gathering power, of the light which diffused out from the side of the flask.

After 23 hours' exposure, a plate was obtained, on which, as was expected, the spectrum of the incident light was very strong. But in addition, two very sharp faint lines occurred on the plate, which did not belong to the mercury spectrum.

These on measurement were found to correspond to wave-numbers 23651 and 21885. These correspond to shifts of 1053 and 1052 from exciting wave-numbers 24704 and 22937, which would involve a wave-length of $9{\cdot}52\mu$.

In order to confirm that these lines were modified lines, the experiment was repeated with conditions unchanged except that potassium bromide crystals of approximately the same degree of coarseness of powdering were substituted for the potassium nitrate crystals. There were no new lines observable on the plate, but the mercury lines were of the same strength as those on the KNO_3 plate.

According to Schaefer [4] the group NO_3 has an inactive fundamental frequency at about 9μ, which comes out strongly in the Raman spectrum.

It would seem reasonable, then, to attribute the wave-length 9.52μ to the inactive fundamental frequency of the NO_3 group.

It is intended to continue this work, investigating the modified radiations diffused from powdered crystals and to extend the method to fine powders.

[4] *This volume*, p. 841.

University College,
Leicester.

GENERAL DISCUSSION.

On Papers in Part II.

THE RAMAN EFFECT.

Professor Victor Henri (*Zürich*), said: In expressing the great enthusiasm with which all have listened to the communication of Sir Venkata Raman, I should like to make a few remarks.

(1) Sir Venkata proposes to represent the production of the bands of the Raman spectrum by the scheme of potential energy suggested by Franck. I am entirely in agreement with this manner of representation which is much more convenient and accounts for the facts better than the idea of energy levels which is very often used by other authors. It is important to remember always that polyatomic molecules react as a whole and that one ought not to be too ready to distinguish the vibrations characteristic of the different groups of atoms. In many respects the same idea has dominated the group of researches on the

ultra-violet absorption spectra which we have conducted for several years on polyatomic molecules.

(2) The Raman spectrum, in the case of polyatomic molecules, has been the key to the analysis of the ultra-violet absorption spectra, which are often absolutely inexplicable. In every case when we study the ultra-violet absorption spectra we now systematically make also a Raman spectrum of the substance; we find that the frequencies obtained by the Raman spectrum are always reproduced with great precision in the ultra-violet spectrum, thus allowing us to recognise what are the fundamental frequencies of inactivated molecules, so that we can classify the absorption spectra of vapours.

In this way M. Langseth has been able to analyse the absorption spectrum of chlorobenzene, Mr. Shapiro that of benzene vapour, M Almasy that of benzaldehyde vapour, M. Köffler that of carbon bisulphide, and ourselves with Mr. Howell that of phosgene. In all these cases the analysis has been made possible, thanks to a knowledge of the Raman spectrum.

(3) With regard to Professor Menzies' communication, I would mention that Professor Baer has obtained this summer at Zürich the Raman spectra of a whole series of solid organic and mineral substances by using these solid substances in the state of powder. One very readily obtains the Raman lines of powdered solid bodies after an exposure of only two or three hours. Professor Baer has thus been able to study the spectrum of the same substance in the solid, liquid and dissolved states. For bodies such as naphthalene he has found that there is no difference in the three cases, whilst for bodies such as nitrate of sodium there is, however, a difference between the spectrum of the solid and that of the solution.

Professor O. W. Richardson (*London*), said: I should like to join in the chorus of appreciation both of Professor Raman's great discoveries and also of the remarkable way in which he has presented them to us. Whilst I do not wish to appear as a critic of the master in this field, I confess to some surprise that he did not tell us more about the observations of MacLennan and McLeod on the Raman effect in hydrogen. To me those experiments seemed very important. They showed that hydrogen when cooled down to low temperatures consisted of a mixture of two kinds of molecules, one in the lowest rotational state ($m = 0$) and the other in the lowest but one ($m = 1$), with the $m = 1$ state preponderating. They formed, in fact, an optical anticipation of much of the work of Bonhoeffer which the newspapers have recently been telling us so much about.

Professor Grimm (*Ludwigshafen*), said: With regard to the diagram of the Raman spectra of PCl_3, $AsCl_3$, $SbCl_3$, and $BiCl_3$ projected by Professor Raman, I should like to observe that the wave-lengths of comparable spectral lines show a gradation similar to that number of other physical properties; from this we can deduce an important influence of the atomic or ionic radii of the central atoms upon the Raman spectra. Thus, it is surely not an accident that there is only a slight difference in the wave-lengths of comparable lines between antimony and bismuth chloride, while there is a greater one between arsenic and antimony chloride. The similarity in the size of the antimony and the bismuth atom is connected with the "*Lanthaniden* contraction" (so called by V. M. Goldschmidt), *i.e.*, with the reduction of the atomic radius found in the rare earths—which, in its turn, is connected with the filling-up of the N-level from 18 to 32 electrons. It may be pre-

dicted with some degree of probability that there will be a greater difference between the arrangement of comparable spectral lines for NCl_3 and PCl_3 than between PCl_3 and $AsCl_3$. Furthermore, it is likely that similar relationships will be found in the series CCl_4, $SiCl_4$, $GeCl_4$, $SnCl_4$, $PbCl_4$, as in the elements of the fifth group.

Professor Schaefer (*Breslau*), said: May I be allowed to make some remarks upon the paper of Sir Venkata Raman?

(1) The same investigations, which have been carried out by Krishnan were also made in my Institute in Breslau, and a preliminary note was sent to the *Physikalische Zeitschrift*. We knew then nothing about Krishnan's work and therefore no reference to it could be made.

(2) Our results are in very good agreement with those of Krishnan; so far as I can see they only differ in one point, *i.e.*, the Raman lines of pure fluid water and crystal water in gypsum. For very well purified water Dadieu and Kohlrausch found not *three* broad bands at about 3μ, but only *two*. In agreement with this we found only two very narrow bands of crystal water at the same wave-length, while Krishnan (also in gypsum) found three. It seems difficult to explain how three bands could exist; the occurrence of a doublet could perhaps be interpreted as a coupling effect due to the association of H_2O molecules.

In this connection, it may be remarked that Dr. Schubert and I found in an investigation of several alums that the water band at about 3μ was a doublet, and the same is valid according to the investigation of K. Brieger for the band at about 6μ.

The President (**Professor T. M. Lowry**, *Cambridge*), asked whether the phenomenon cited by Professor Menzies, in which scattered light appeared to be emitted by an oscillator vibrating at right angles to the oscillation set up by the incident light, was related in any way to the optical rotatory power of quartz. He asked the question because, according to the modern theory of optical rotatory power, as developed by Born, Lande, and Werner Kühn, this phenomenon depends on the existence in the medium of oscillators coupled in such a way that the vibration of one produces in the others a component vibration in a direction at right angles to that of the first, so that when A moves along the axis of x, B moves also along the axis of y or z or both. This relation might perhaps be checked by comparing sodium chlorate, of which he had some fairly large crystals, with analogous crystals which are devoid of optical activity.

Professor R. Mecke (*Bonn*), said: I should like to complete the table

NH_3	*g*	933*	966*	1630*		3336			
	l	107–		158–		(3212)	3214	3298	
H_2O	*g*	—		1600*			3735*	3850*	
	l	—		—		3200	3453	3610	
CH_4	*g*	—		—		2914	3071	3022	
	l	—		—		2908	?	?	
C_2H_4	*g*	1342		1623		2880	3019	3240	3272
	l	134–		162–		300–	308–	?	?
SO_4	Aq.	450	608	989	1218	—	—	—	—
SO_4	conc.	404	557	923	1133	1317	—	—	—

The data marked * are taken from investigations of infra-red spectra (*cf.* p. 936), the other lines from a paper of Dickenson, Dillon, and Rasetti on the Raman spectra of polyatomic gases, *Physical Rev.* **34**, 582, 1929 (NH_3 liquid, CH_4, C_2H_4), Ganesan and Venkateswaran, *Indian J. Physics*, Vol. IV., Part III. No. 14, 1929 (H_2O), for SO_4, see also the paper by Taylor, page 833.

published in Professor Daure's paper, by making use of some new data on the analysis of infra-red bands and on the Raman lines of polyatomic gases.

For ammonia the shift of the frequencies is quite distinct, although it is in the opposite direction for the first frequency. It seems to me that the doubling (tripling ?) of the frequencies in the case of the liquid ammonia represents an accentuation of the energy difference due to the symmetrical and antisymmetrical levels. For the highly associated molecule of liquid water the shift is still greater, as is also the case for concentrated sulphuric acid. I do not think that methane and ethylene show any changes, neither do liquid hydrogen, nitrogen, and oxygen as was shown by McLennan (p. 797).

Professor J. Errera (*Brussels*), said that in confirmation of the opinion of Professor Sir C. V. Raman on the influence of molecular association one might add that the work of Ramdas accords with the results of Professor Debye, who has shown that the dipolar molecules of ether in the liquid state are not associated : it was thus easy to see why Ramdas found the same Raman lines in the vapour state as in the liquid state.

Professor W. E. Garner (*Bristol*), said : The flame spectra of combustible gases containing carbon compounds give two prominent emission bands at 2·8 and 4·4μ corresponding to the two absorption bands of carbon dioxide at 2·70 and 4·25μ. These bands broaden as the temperature and pressure of the flame is increased. The band at 2·8μ broadens symmetrically, so that the maximum is not displaced, but that at 4·4μ broadens unsymmetrically. The wave-length of the maximum emission shifts to longer wave-lengths. The unsymmetrical broadening may be due to the presence of radiation corresponding to the Raman band for carbon dioxide which is found at 4·64μ. In an explosion spectrum of carbon monoxide and oxygen, the intensity of the radiation at 5·0μ is practically the same as that at 4·2μ, which is possibly due to the occurrence of the 4·64μ band in emission.

Dr. Menzies : I am greatly interested in Professor Henri's statement that Professor Bär in Zürich has independently found that Raman spectra may be obtained using powdered crystals, as it confirms my own investigations. I shall look forward to reading an account when it is published.

PART III.(A).—THE INFRA-RED SPECTRA OF SOLID BODIES.

INTRODUCTORY PAPER.[1]

By Professor Clemens Schaefer (*Breslau*).

Received 12th August, 1929.

I.

By solid bodies we understand only those crystals the nature of which is determined by the following propositions (which can be regarded as the result of modern experimental investigations) :—

(*a*) The lattices of crystals are built up according to determined laws by the separate nuclei of the atoms and by the separate electrons. Both kinds of particles play the same rôle in the lattice and act one upon the other with forces of equal kind.

(*b*) The lattice consists of a periodic repetition of a group of nuclei and electrons in space ; this group, which we may call the " Basisgruppe," is electrically neutral, *i.e.* it contains as many positive as negative charges.

(*c*) There may be in the " Basisgruppe " S particles in all, p of which may be nuclei, $(S - p)$ electrons ; in this case we say that the crystal is " p-atomic."

Such an aggregate of particles possesses definite free vibrations, and the fact that the individual masses of the " Basisgruppe " carry electrical charges of different sign makes it possible for some of these frequencies to be excited by light waves, *i.e.* by periodic external electromagnetic forces.

There exists a theorem as to the number of infra-red vibrations, as first pointed out by M. Born.[2]

(*d*) If the " Basisgruppe " contains p nuclei, then the maximum possible number of infra-red internal vibrations is $3(p - 1)$.

This number of infra-red frequencies can only exist in the case of bi-axial crystals ; with the uni-axial there exist only $2(p - 1)$ and, finally, with the regular crystals only $(p - 1)$ infra-red frequencies ; in the former case two frequencies coincide on account of the greater symmetry ; in the latter, three.

It follows from the above-stated theorem that in a regular diatomic

[1] In writing this paper, it was not my purpose to give a full account of the whole of the infra-red work on solid bodies ; on the contrary, I have selected those parts which seemed to me of special value for the investigation of molecular structure. The report has, therefore, received a somewhat subjective treatment ; those who wish fuller information may refer to the excellent little book by Rawlins and Taylor, *Infra-red Analysis of Molecular Structure* (Cambridge, University Press, 1929), or *Le Spectre Infra-rouge*, by Lecomte (Presses Universitaires de France, 1928). Perhaps I may be allowed to add that Dr. Matossi and I have also finished a book on the infra-red spectrum (Berlin, Springer), which will, as I hope, be published at the end of the year.

[2] M. Born, *Dynamik der Kristallgitter*, § 19, 1915.

crystal (NaCl, KCl, LiF, NaF, etc.) we can only find *one* infra-red frequency, in excellent agreement with experience.

II.

According to theorem (*d*) of Section I. the maximum possible number of frequencies is limited; in general one finds experimentally fewer frequencies than are theoretically possible. This arises from the fact that, on account of the existence of symmetries, several frequencies may coincide; an example of this kind was given at the end of Section I. It may also happen, that on account of the symmetries an actually existing vibration cannot be excited by external periodic forces of the same frequency. This is the case when the movement of the particles is not accompanied by a variation of the electric moment. Such a vibration we may call *optically inactive*. Nevertheless it seems possible, as will be shown later, to determine those inactive vibrations in a somewhat indirect way.

III.

The forces acting on a moving particle of the crystal depend on the displacements, which the neighbouring particles undergo from their equilibrium positions; if the forces are linear functions of these displacements (*i.e.* if Hooke's Law is valid) the vibration is said to be *harmonic*. This will be the case only when the amplitudes are infinitely small. This was tacitly supposed in the foregoing explanations and theorems; the correctness of theorem (*d*) of Section I. as to the greatest possible number of vibrations, in particular, holds only in this case of infinitely small amplitudes: we shall call the actual frequencies in this case the *fundamental vibrations* or shortly the *fundamentals*.

If the amplitudes become greater, the forces will in general depend on the squares and the cubes of the displacements, and in these cases the vibrations are said to be *anharmonic*. We call the vibration *symmetrical* if the force depends on the odd powers of the displacements; on the other hand it is said to be *unsymmetrical* if the expression for the force contains only the even powers. If the forces are consistent with Hooke's Law, then the vibrations are of course always symmetrical; if this is not the case, they may be either *symmetrical* or *unsymmetrical*.

An example may illustrate this: a diatomic crystal has only *one* fundamental of frequency ν_0, if the amplitudes are infinitely small; for finite amplitudes, if the *squares* of the displacements occur in the expression for the force, then we have, in addition to the fundamental, the whole series of "harmonic overtones," *i.e.* vibrations of frequency $2\nu_0$, $3\nu_0$, . . . etc. In the special case when, for finite amplitudes, the members with squares of displacements are missing and only the cubic members are present, we find only the *odd* overtones, *i.e.* the supplementary frequencies $3\nu_0$, $5\nu_0$, . . . etc.

Analogous conditions hold in more complicated cases. If the crystal possesses the following infra-red fundamentals

$$\nu_1, \nu_2, \nu_3, \ldots \nu_\lambda \quad . \quad . \quad . \quad . \quad (1)$$

we have, with finite amplitudes, the following "combination-tones":

$$\nu = \pm p_1\nu_1 \pm p_2\nu_2 \pm \ldots \pm p_\lambda\nu_\lambda \quad . \quad . \quad . \quad (2)$$

where $p_1, p_2 \cdots p_\lambda$ are positive integers.

Of special interest is the case when one (or several) of the fundamentals is *optically inactive, i.e.* when it does not manifest itself directly in the usual manner. It is then possible for such an inactive fundamental vibration to combine with another *active* fundamental and thus to produce an *active* combination frequency. If this is the case—and it can be experimentally tested—then we are able to find indirectly the inactive fundamental. We shall discuss later how this has been effected in special cases.

IV.

In the foregoing we have tacitly identified the frequency of the electromagnetic radiations with the frequency of the mechanical vibration. This corresponds with the views of classical electrodynamics ; but these have been proved to be incorrect and inapplicable to atomic processes such as absorption, reflection, and dispersion. It is therefore necessary to justify the foregoing statements from the standpoint of the Quantum Theory.

We shall adopt in the following pages the language of the *older* form of the Quantum Theory. According to this the electromagnetic system, which is here represented by the crystal-lattice, is capable of different states, to each of which belong discrete values of energy E, say E_0, E_1, E_2 . . . E_n, E_{n+1} . . .

If we consider first an harmonic oscillator of frequency ν_0, which carries an electrical charge, then the Quantum Theory leads to the conclusion, that

$$E_n = n \cdot h \cdot \nu_0 \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

where n is a positive integer, h Planck's constant, and ν_0 the frequency of the mechanical vibration. Since, according to Bohr's equation the frequency ν_{qu} of the emitted or absorbed wave during a transition of the system from the state n to n' is

$$\frac{E_n - E_{n'}}{h} = \nu_{qu} \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

and since, according to the correspondence-principle, the quantum number n can only vary by ± 1, it follows that $n - n' = \pm 1$ itself, and therefore for the harmonic oscillator, taking account of (3) and (4) :

$$\nu_{qu} = \nu_0.$$

Thus, the frequency of the electromagnetic radiation of an harmonic oscillator is, according also to the Quantum Theory, identical with that of the mechanical vibration, as it was the case in the classical theory.

The situation is slightly different, if we have to do with an anharmonic oscillator. Then instead of (3) we have for the different possible energy levels :

$$E_n = nh\nu_0 + \alpha\nu_0 \cdot n^2 + \ldots \qquad . \qquad . \qquad . \qquad (5)$$

where α depends on the law of the mechanical force acting on the particle (see above Section III.). If the system "jumps" from the state with quantum number n to n', we have according to (4) :—

$$\frac{E_n - E_{n'}}{h} = \nu_{qu} = (n - n')\nu_0 + \alpha\nu_0(n^2 - n'^2) \qquad . \qquad . \qquad (6)$$

At ordinary temperatures there exists only the normal state of the system, which has the quantum number $n = 0$; but in this case n can vary by an

arbitrary integer: the system can "jump" to the state $n' = 1$, $n' = 2$, etc. From the last equation we find for the frequencies in these different cases:

$$0 \rightarrow 1 : \nu_{qu} = \nu_0(1 + \alpha),$$
$$0 \rightarrow 2 : \nu_{qu} = 2\nu_0(1 + 2\alpha),$$
$$0 \rightarrow 3 : \nu_{qu} = 3\nu_0(1 + 3\alpha) \ . \ . \ .$$

That is to say, if we neglect for a moment the member with α (which is generally small) we find the whole series of harmonic overtones for the anharmonic oscillator, *i.e.* the same result as according to the classical theory. Strictly speaking this is not correct, on account of the member with α; but since in most cases the correction is only slight we need not take it into consideration in the following pages, so that there is, in this case also, no practical difference between the Quantum Theory and the classical views.

We are therefore entitled to use the language of the classical theory, which is perhaps more convenient for some readers.

V.

There are in the main three methods of observing free vibrations in solid bodies, *i.e.* the method of reflection, of absorption and of dispersion.

(*a*) The first method (reflection) depends upon the circumstance that the reflection power of a (non-metallic) crystal generally has low values which, nevertheless, increase rapidly in the immediate neighbourhood of a strong vibration. The maxima of the reflection curve therefore show us—approximately—the wave-lengths of the vibrations. With *one* limitation: the free vibration must be a *strong* one; if this is not the case, then the reflection curve is not sensibly altered and the method fails. That is to say, with the method of reflection we can only find the strongest oscillations of the crystal (and these will in general be the *fundamentals*) while the combination-frequencies, (which are much weaker) cannot be found in this manner. This method therefore proves very useful for a first survey of the unknown spectrum and for finding the fundamentals only.

A special case of the method of reflection is the well-known method of the "residual rays" developed by H. Rubens.[3] It consists, briefly, in a repetition of the process of reflection and is therefore even less sensitive than the simple method of reflection; it does not generally yield all the fundamentals, but only the strongest of them. The special value of the method of the residual rays lies in that with its aid it was possible to get very long infra-red wave-lengths.

(*b*) Far more sensitive is the investigation of vibrations by the second method, the determination of the absorption or the transmission; for, from the form of the absorption-law, it follows that every absorption, however small, can be detected by using sufficiently thick pieces of the material in question. The minima of the absorption- or transmission-curve coincide almost exactly with the wave-lengths of the free vibrations. From this it follows that by this method not only can the fundamentals be found, but also all the combinations. The absorption spectrum is therefore generally far more complicated than the reflection spectrum. If one has measured the absorption- and the reflection-spectrum of a substance—the latter giving only the fundamentals $\nu_1 \nu_2, \ . \ . \ . \ \nu_\lambda$—then it

[3] H. Rubens and E. F. Nichols, *Wied. Ann.*, 60, 418, 1897.

should be possible, to express all other vibrations ν in the form of the equation (1). If this can be effected, one can be sure that the reflection-method has really yielded all the fundamentals and that all the other vibrations are combinations from these fundamentals.

But if there remain frequencies which cannot be brought into the form (1), where the ν_λ are the fundamentals found by reflection, then it may be possible that there exists, also, a fundamental which is *inactive ;* let us call its frequency x. We must, therefore, write instead of equation (2) the following :

$$\nu = \pm p_1\nu_1 \pm p_2\nu_2 \pm \cdot \cdot \cdot p_\lambda\nu_\lambda \pm Px, \quad . \quad . \quad (7)$$

where P is a positive integer. If all equations of this kind furnish the same value of x—of course it may be that more than one inactive fundamental exists—there is strong evidence that x is really the frequency of an inactive, *i.e.* imperceptible, fundamental, which in this indirect manner has been found.

VI.

A third method for getting the free vibrations is the measurement of the dispersion of the substance in question. For from the theory of dispersion it follows that the dispersion depends on the wave-lengths of the free vibrations, since dispersion is a resonance phenomenon. The method has the disadvantage that it demands very laborious numerical calculations and furnishes only roughly approximate results, since the dispersion is not much altered when the resonance wave-lengths are varied. Historically the method was of great importance, as it led Rubens in 1897 to his famous method of residual rays.

A further success can be attributed to the method of dispersion. The measurement of dispersion for quartz in connection with the theory led to the conclusion, that quartz becomes highly transparent for wave-lengths beyond 50μ, while it is opaque for the lower infra-red radiation beginning with 4μ ; the index of refraction for these longer wave-lengths is about 2·15, *i.e.* far greater than for the extreme ultra-violet. A quartz lens therefore has, for very large infra-red wave-lengths (beyond 50μ), a much shorter focal distance than for all other radiations. This " chromatic error " of quartz lenses can be used to separate the long waves from the shorter, as Rubens and Wood [4] showed in 1910 ; this method (*Quarzlinsenmethode*) has indeed proved to be very successful for the isolation of waves up to $\frac{1}{3}$ mm., as will be mentioned later in fuller detail.

VII.

After this brief account of the available methods we pass to the first measurements of the infra-red spectrum of solids.

These were measurements of the indices of refraction for quartz, fluorspar, rocksalt and sylvite, since these materials are the only ones with a sufficient transmissivity in the infra-red to enable them to be used as prisms. The pioneers in this region were, above all, Langley, Rubens, Paschen, Snow, and Trowbridge.[5] They measured the indices

[4] H. Rubens and R. W. Wood, *Ber.*, p. 1122, 1910.

[5] S. P. Langley, *Wied. Ann.*, **22**, 598, 1884 ; *Ann. Chim. et Physique*, **9**, 484, 1896 ; *A. Smithson Instit.*, Vol. I., 1902 ; H. Rubens, *Wied. Ann.*, **45**, 238, 1892 ; H. Rubens and B. Snow. *Wied. Ann.*, **46**, 529, 1892 ; H. Rubens, *Wied. Ann.*, **53**, 267, 1894 ; H. Rubens and A. Trowbridge, *Wied. Ann.*, **60**, 724, 1897 ; F. Paschen, *Wied. Ann.*, **53**, 301, 1894 ; *Ann. Physik*, **4**, 299, 1901 ; **26**, 120, 1908 ; **35**, 1005, 1911.

of refraction of these four substances as far and as accurately as possible; the knowledge of the indices allowed then the calibration of the prism-deviation in terms of wave-lengths. At the same time the transmission of these substances was investigated. The practical result is as follows: a prism of quartz cannot be used beyond 4μ, a prism of fluorspar not beyond 9μ, rocksalt absorbs all radiation beyond 14μ and only sylvite prisms can be used up to 22μ. In the region from 1 to 4μ quartz has the greatest dispersion and furnishes therefore—under equal conditions—the greatest resolving power; then follows fluorspar for the region from 4 to 9μ, rocksalt from 9 to 14μ, and lastly sylvite for the region from 14 to 22μ. The spectral region up to 22μ, which can be attained in this manner with prismatic resolution, is often called *the short wave region.*

VIII.

Longer wave-lengths can be isolated with the Rubens method of residual rays. The following fundamentals for diatomic crystals were determined in this way (Table I.):—

TABLE I.

Substance.	Fundamental in μ.	Author.	Method.
ZnS	30·9	Rubens[6]	Residual Rays
NaCl	52	,,	,,
KCl	63·4	,,	,,
AgCl	81·5	,,	,,
KBr	82·6	,,	,,
TlCl	91·6	,,	,,
KF	94·1	,,	,,
AgBr	112·7	,,	,,
TlBr	117·0	,,	,,
TlF	151·0	,,	,,

According to the modern theory of crystal-lattices that of NaCl consists of two "simple" face-centred cubic lattices, each of which is formed by Na-ions or Cl-ions. These two lattices are brought together in such a manner that in a NaCl crystal every Na ion is symmetrically surrounded by 6 Cl ions and *vice versa.* With the other diatomic crystals the position is very analogous. The two "simple" lattices can vibrate relatively to another, each lattice behaving nearly as a rigid body. From this symmetrical structure it follows at once, that for finite amplitudes the vibration may be *anharmonic* but cannot be *unsymmetrical;* the squares of the displacements cannot in this case enter into the expression of the force. If "overtones" exist, the first possible, the octave of the fundamentals, cannot occur. This is a point of importance, as will be shown later when we discuss the absorption spectra in fuller detail.

Regarding the figures of Table I., it is to be borne in mind that the cited values of the wave-lengths of the fundamentals are not exact, because the reflection maximum does not coincide exactly with this

[6] H. Rubens, *Ber.*, 513, 1913, and 4, 1915; H. Rubens and H. v. Wartenberg, *Ber.*, 69, 1914.

wave-length. The difference may be considerable; it can be computed in some cases, as has been pointed out by Försterling.[7]

An interesting question arises as to the fundamentals of mixed crystals, *i.e.* of a mixed crystal of NaCl and KCl. The fundamentals of the components are known (approximately 52μ and $63{\cdot}4\mu$; see Table I.); does the mixed crystal show both these fundamentals (perhaps in different strength with varying concentration) or does it show only *one* new fundamental? This question was answered in the latter sense by an investigation of Krüger, Reinkober, and Koch-Holm;[8] there exists only *one* fundamental in mixed crystals of this type. Mixtures of NaCl + KCl, KCl + RbCl, KCl + TlCl were investigated; the wave-length of the "resultant" fundamental lies *between* the wave-lengths of the original fundamentals, and is shifted linearly from the one position towards the other, when the concentration of the one component is increased.

IX.

By using the quartz lens method Rubens and v. Baeyer[9] have isolated the greatest known infra-red wave-length; a mercury-arc burning in fused quartz yields a complex radiation, from which a wave-length of 313μ or nearly $\frac{1}{3}$ of a millimetre could be isolated. In other cases, *i.e.* from the Auer burner, there was found[10] by the same method a wave-length of nearly 100μ.

By combining the method of residual rays with that of quartz lenses, Rubens[11] was also able to find in the "long wave spectrum" of calcite a fundamental at 94μ.

These examples will suffice to show the efficiency of the methods described.

It is scarcely necessary to point out the importance of a knowledge of the factors which govern the behaviour of other crystal properties, *i.e.* specific heat, the melting-point, etc.

X.

Things become more complicated when we proceed to crystals which contain more than 2 nuclei in the "Basisgruppe," *i.e.* the carbonates, the nitrates, the sulphates, etc.

If we examine, for example, several sulphates by means of the reflection method, we find for all of them two fundamentals in the short wave region at the approximate wave-lengths of 9μ and 16μ. In the same manner we find for the carbonates three fundamentals in this region at approximately 7μ, 11μ, and 14μ. The same is the case with the nitrates, which show a strong analogy with the carbonates: here one finds also three fundamentals, which are only shifted a little to greater wave-lengths as compared with the carbonates. Up to the present the following groups have been investigated, *viz.* Sulphates, Carbonates, Nitrates, Selenates, Chromates, Chlorates, Iodates, Metasilicates,[12] and the NH_4-

[7] K. Försterling, *Ann. Physik*, **61**, 577, 1920.
[8] F. Krüger, O. Reinkober, and E. Koch-Holm, *Ann. Physik*, **85**, 110, 1928.
[9] H. Rubens and O. v. Baeyer, *Ber.*, 339 and 666, 1911.
[10] H. Rubens and R. W. Wood, *Ber.*, 1122, 1910.
[11] H. Rubens, *Verh. deut. physik. Gesellschaft*, **13**, 102, 1911.
[12] Cl. Schaefer and M. Schubert, *Ann. Physik*, **50**, 283, 1916 (Carbonates and Sulphates); *Ann. Physik*, **55**, 557, 1918 (Nitrates); *Z. Physik*, **7**, 309, 1921 (Chlorates, Bromates, Iodates); *Z. Physik*, **7**, 297, 1921 (Chromates, Selenates); *Z. techn. Physik*, **3**, 201, 1922 (Metasilicates); G. Laski, *Z. Kristallograph*, **65**, 607, 1927 ($NaClO_3$ and $NaBrO_3$).

group.[13] The latter has three fundamentals (at 3·20, 5·85 (very weak), and 6·69μ). Those at 3·20 and 6·69 occur also in the absorption spectrum of *natural sylvite*, while artificial sylvite has no absorption at all in this spectral region.[14] The absorption of natural sylvite is due to a little impurity of NH_4Cl.

The first characteristic is that these fundamentals are identical for each radical-ion, *i.e.* SO_4, CO_3, NO_3, etc. It follows that the fundamentals *belong* to these groups respectively.

It is further characteristic that the wave-lengths of fundamentals in the above-mentioned (and analogous) cases are almost independent of the nature of the cation,—if we leave out of question an insignificant shift of the wave-length with increasing atomic weight of the cation. Although there cannot be doubt that the fundamentals now being considered are special vibrations of the crystal-lattice, it is possible to simplify the consideration by supposing that the conditions are just the same as if there were only *one* group, *i.e. one* SO_4-, CO_3-, or NO_3-group. Vibrations of such a kind (where the centre of gravity of the chemical radical is at rest, while the constituent particles oscillate) we shall call *internal vibrations*, to distinguish them from "external" vibrations, which occur when the cation-lattice and the radical-lattice vibrate against one another, the lattices being regarded as nearly rigid bodies.

It follows at once from this consideration, that the "internal" vibrations lie in the short wave-region (or in the immediate neighbourhood), while the external vibrations—on account of the larger masses and smaller forces—belong to the long wave region.

We shall occupy ourselves in the following paragraphs with the above defined *internal* vibrations.

XI.

A first consequence to be inferred from the above data is that the groups in question are on the whole of the same shape and of approximately the same dimensions in all the crystals in which they occur. We may, therefore, conclude that in all sulphates the SO_4-group is nearly the same, etc. It may be worthy of remark that this accords well with the results of modern Röntgen-Analysis.

We can now, also, examine to some extent the statement of Born's theorem (*d*) of Section I. on the greatest possible number of fundamentals, if we regard the internal vibrations as (nearly) independent of the other vibrations of the crystal-lattice. According to this theorem we might expect that the number of fundamentals found in a regular crystal is, in general, doubled if we pass to an uni-axial crystal, and tripled in bi-axial ones. This is in fact the case with the sulphates (and selenates): for in the regular sulphates we have two fundamentals at approximately 9μ and 16μ; in the uni-axial sulphates we find that every fundamental has doubled, the two components lying very near together, and in the bi-axial every fundamental is split up into three narrow components.

It is, however, not to be expected that this should be always the case, because, on account of the symmetries, the number of fundamentals is often smaller than the theoretically possible number; this is found, for instance, in the case of the carbonates.

[13] O. Reinkober, *Z. Physik*, **3**, 1, 1920; and **5**, 192, 1921.
[14] Cl. Schaefer and C. Bormuth, *Z. Physik*, **50**, 363, 1928.

XII.

We get further details, if we examine the manner in which the fundamentals are associated with the principal crystalline directions, *i.e.* if we examine them by polarised light. This applies of course only to the case of uni-axial and bi-axial crystals.

If we take for instance the sulphates (which in the regular crystal form have two fundamentals—see above Section XI.—which are split up into two narrow components in uni-axial crystals), examination with polarised radiation shows that the one of these components belongs to the ordinary ray, while the other correponds to the extraordinary : the one vibrates normally to the axis, the other parallel with it.

In bi-axial crystals we distinguish the three directions of the greatest, smallest and of the intermediate refractive index, which are generally designated by *a*, *b*, *c* respectively. The fundamentals of the sulphates are in this case tripled, and each component-vibration is directed parallel to one of these axes respectively.

The state of affairs in the case of the carbonates is somewhat different. A regular carbonate—Northupite—shows the three above-mentioned fundamentals at nearly 7μ, 11μ, 14μ. Closer examination of the uni-axial carbonates of calcite-type with polarised light reveals the fact, that the vibrations at 7μ and at 14μ belong to the ordinary ray, i.e. are directed normally to the axis, while that at 11μ vibrates parallel with the axis, *i.e.* belongs to the extraordinary ray.

This is easily explained if we investigate the mechanical vibrations, which the CO_3-group can undergo. According to the famous researches of the Braggs with Röntgen-Rays, the structure of the CO_3-group in the carbonates is as follows : the four atoms of the group (C, 3O) lie in a plane, the three O-atoms at the corners of an equilateral triangle, the C-atom at its centre of gravity ; the plane of this configuration stands normally to the direction of the principal axis of the crystal.

Brester[15] and Kornfeld[16] have investigated the mechanical vibrations which such a system of four particles in such a configuration can undergo. There exist *firstly* two fundamentals of different frequency *in* the plane of the group, without definite direction of vibration in this plane, and *secondly* a vibration *normal* to the plane of the group with a frequency which is intermediate between the two first mentioned. That is, we have two fundamentals belonging to the ordinary and one belonging to the extraordinary ray ; the former may be identified with the observed vibrations at 7μ and 14μ, the latter with that of 11μ. So it seems as if there were a very good coincidence of the experimental results with the theoretical expectation.

But there is a difficulty, for experiment has decisively shown that the maxima at 7μ and 14μ for calcite are doublets, and the same seems to be true for the other uni-axial carbonates.[17]

So we have, in fact, not two simple fundamentals belonging to the ordinary ray, but *two pairs* of fundamentals. This is not consistent with the assumption that the 3O-atoms of the CO_3-group lie at the corners of an *equilateral* triangle. But if we imagine (with Brester) the triangle to be a little distorted (*e.g.* an isosceles triangle differing very little from an

[15] C. J. Brester, *Kristallsymmetrie und Reststrahlen*, Diss. Utrecht, 1923.
[16] H. Kornfeld, *Z. Physik*, **26**, 205, 1924.
[17] Cl. Schaefer and M. Schubert, *Ann. Physik*, **50**, 283, 1916 ; Cl. Schaefer, F. Matossi, and F. Dane, *Z. Physik*, **45**, 493, 1927.

equilateral), then we find theoretically that two pairs of fundamentals exist, of definite direction of vibration : the one component of each pair vibrates parallel to the base of the triangle, the other perpendicular thereto. The distortion can only be small, so that it cannot be detected by Röntgen-Analysis. In fact such a distortion does take place in the *bi-axial* carbonates (Witherite, Cerussite) ; in this case also it cannot be found by Röntgen-Analysis.

The foregoing shows the fruitfulness of infra-red work for the purpose of determining the molecular structure : such work can serve to control, to correct and to complete the researches with Röntgen-Rays.

The uni-axial nitrates behave somewhat differently ; in this case, also, I am inclined to suggest slight corrections of the result which Röntgen-Analysis has furnished as to the structure of the NO_3-group.

One point of importance remains to be discussed. In addition to the three fundamentals of the CO_3-group, of which we have just been speaking in the foregoing (we leave out of question, for a moment, the fact that two fundamentals are doublets), there exists a *fourth fundamental which is optically inactive ;* it corresponds to the following mechanical vibration : the C-atom in the centre of gravity does not move at all ; the 3O-atoms oscillate in straight direction to and fro from the C-atom. Therefore the electric moment is at every instant equal to zero, *e.g.* it is not altered by this vibration, which therefore cannot be examined in the direct usual manner. We shall revert later to this inactive fundamental.

XIII.

So far we have been concerned only with the fundamentals of some chemical radicals ; but since the particles have in general finite amplitudes, it is to be expected that there will exist, in addition to the fundamentals, weaker combination-frequencies, which can be found by the more sensitive method of absorption. Up to the present a detailed study of this kind has only been made in the case of the CO_3-group. Schaefer, Bormuth, and Matossi [18] examined the absorption-spectrum of the following carbonates : $MgCO_3$, $CaCO_3$, $FeCO_3$, $(MgCa)CO_3$, $BaCO_3$, $PbCO_3$, while Rawlins, Taylor, and Rideal [19] made an analogous research on $SrCO_3$; the pieces under examination were cut perpendicularly to the principal axis (with bi-axial crystals perpendicularly to the acute bisectrix). In my laboratory there has also been carried out a (hitherto unpublished) investigation on the absorption-spectrum of some nitrates, especially of $NaNO_3$, of which we shall speak later.

The absorption-spectra of the above cited carbonates are very similar one to another, so that it is impossible at first sight, to distinguish them. One finds a disturbingly great number of absorption minima, the wave-lengths of which are indicated in Table II.

According to the general considerations of Section III., it should be possible to express the combination-frequencies ν in the form :

$$\nu = \sum_{s}^{1\cdot 3} p_s \nu_s \quad . \quad . \quad . \quad . \quad . \quad (8)$$

[18] Cl. Schaefer, C. Bormuth, and F. Matossi, *Z. Physik*, **39**, 648, 1926.

[19] F. I. G. Rawlins, A. M.Taylor, and E. K. Rideal, *Z. Physik*, **39**, 660, 1926 ; F. I. G. Rawlins and E. K. Rideal, *Proc. Roy. Soc.*, A. 116, 140, 1927.

TABLE II.

Fundamentals.	$MgCO_3$.*		$CaCO_3$.		Dolomite.*		$FeCO_3$.*		$BaCO_3$.*		$PbCO_3$.	
$\nu_1 \perp$	6·69μ		6·7, 7·0		6·9		6·77		6·85		7·04, 7·28	
$\nu_2 \perp$	13·78		14·16		14·7		13·54		14·48		15·00	
ν_0	9·39		9·10		9·19		9·33		9·57		10·10	
$\nu_3 \parallel$	11·25		11·38		11·45		11·53		11·61		12·00	
Combin.	Comp.	Obs.	Comp.	Obs.	Comp.	Obs.	Comp.	Obs.	Comp.	Obs.	Comp.	Obs.
$2\nu_1$ . .	3·48	3·47	3·50	3·47	3·57	3·50	3·36	3·41	3·49	3·525	3·64	3·67
	3·34	3·33	3·35	3·35	3·45	3·38			3·42	3·455	3·52	3·60
$\nu_1 + \nu_2$.	4·62	4·60	4·64	4·64	4·82	4·63	4·41	4·60	4·70	4·75	4·90	4·92
	4·53	4·46	4·52	4·50?	4·71	4·56	—	4·3?	4·65	4·33 ?	4·79	4·68 ?
$\nu_1 + \nu_0$.	3·99	3·94	3·96	3·93	4·02	3·97	3·91	3·91	4·04	3·99	4·23	4·15
	3·88	3·82	3·90	(3·87)	3·93	(3·89)			3·95	(3·92)	4·10	(4·05)
$\nu_2 + \nu_0$.	5·58	5·55	5·52	5·545	5·67	5·58	5·38	5·52	5·77	5·66	6·04	5·80
$\nu_3 + \nu_0$.	5·12	5·10	5·12	5·15	5·09	5·13	5·16	5·15	5·24	5·12	5·49	5·40
$3\nu_1$ . .	2·30	2·33	2·33	2·33	2·38	2·37	2·26	2·34	2·33	2·388	2·43	2·497
	2·23	2·29	2·23	2·30	2·30	3·325		(2·27)	2·28	(2·35)	2·35	(2·44)
$2\nu_1 + \nu_2$.	2·76	2·78	2·80	2·786	2·87	2·92	2·67	2·80	2·82	2·855	2·93	2·928
	2·70	2·73	2·70	(2·74)	2·80	(2·89)			2·77	2·84	2·85	(2·955) ?
$2\nu_1 + \nu_0$.	2·52	2·53	2·53	2·533	2·57	2·57	2·48	2·53	2·56	2·595	2·68	2·677
	2·47	2·48	2·46	(2·5) ?	2·51	(2·53)		(2·485)	2·52	(2·54)	2·62	2·645
$\nu_1+\nu_2+\nu_0$	3·08	3·10	3·10	3·10	3·11	3·14	3·00	3·09	3·16	3·17	3·30	3·26
	3·04	3·05	3·05	3·04	3·16	3·17		(3·05)	3·13	3·16	3·25	(3·28) ?
$\nu_1 - \nu_2$.	13·0	—	12·9	12·7?	13·0	12·9?	14·5	—	13·0	—	13·3	13·68 ?
$2\nu_1 - \nu_0$.	5·20	5·10?	5·31	—	5·53	—	5·31	—	5·34	—	5·41	5·4?
$\nu_1 + \nu_2 - \nu_0$	8·50	8·43	9·0	9·02	9·8	9·85	8·37	—	9·42	9·14	9·13	9·11
$\nu_1 + \nu_0 - \nu_2$	5·46	—	5·34	—	5·37	—	5·68	—	5·52	—	5·74	5·8?

? : Interpretation uncertain ; ( ) : Only slightly indicated ; * : Separation computed from $2\nu_1$.

where the ν_s are the three known fundamentals and the p_s integers. If we take the following fundamentals for the CO_3-group :—

ν_1 : 7μ)
ν_2 : 14μ) (approximate values only ;
ν_3 : 11μ) the exact values are inserted in Table II.).

It is, however, impossible to put all observed combinations in the form of equation (8) : *there remain five vibrations unexplained.* But we must remember (as has been stated at the end of the preceding paragraph) that in the CO_3-group there exists also an inactive fourth fundamental, of course of unknown frequency and wave-length. Denominating its frequency by ν_0, let us try to put the frequencies ν of the combinations in the wider form :—

$$\nu = \sum_{s}^{1\cdot3} p_s\nu_s + p_0\nu_0 \quad . \quad . \quad . \quad . \quad (9)$$

This form covers indeed *all* observed vibrations, if we give to the inactive fundamental a wave-length of about 9μ : the accurate values are indicated at the top of Table II.

Two further remarks may still be offered on this subject :—

(1) As was said in Section X., the nitrates have also three fundamentals in the immediate neighbourhood of the CO_3-fundamentals ; it must be added that there exist an inactive fundamental too. It was therefore to be expected that the absorption-spectrum of the nitrates would be very similar to that of the carbonates, if the whole reasoning is sound at all. In my laboratory this investigation was carried out ; and in fact the absorption-spectrum of the NO_3 group shows a complete coincidence with that of the carbonates, so that it is difficult to distinguish one from another. The resemblance goes so far that the above reasoning for the carbonates also holds for the nitrates. It is necessary to use an equation of the type (9), with an unknown inactive frequency ν_0, to express the combination-frequencies in terms of the fundamentals. The wave-length of the unknown inactive fundamental was found to be about 9μ, as in the carbonates.

(2) It has been doubted whether an inactive vibration can produce, together with an active, an active combination-vibration, and therefore some investigators have not accepted the proposed computation of the inactive fundamental of the carbonates. It may be remarked, however, that in the Raman effect for calcite it is *especially this inactive fundamental which is found in considerable strength in the photographs.* I may add, that in my laboratory the Raman effect of $NaNO_3$ was studied too, with the result that in this case, also, the inactive fundamental at about 9μ appeared very strong on the photographic plate. This seems to me very strong evidence for the correctness of the point of view stated in this paper.

XIV.

The H_2O-group also belongs to the groups which show "internal vibrations" in the sense defined in Section X. It is known that many crystals contain "water of crystallisation," so that with each molecule of the compound there is combined a definite number of H_2O molecules. Now liquid water has vibrations at nearly $3{\cdot}2\mu$ and at $6{\cdot}3\mu$, so that the problem arises, whether the so-called water of crystallisation also, possesses these same vibrations. This is the case, as was shown first by W. W. Coblentz.[20] Later Schaefer and Schubert [21] and K. Brieger [22] investigated this more closely and found that these bands at $3{\cdot}2\mu$ and $6{\cdot}3\mu$ occur in all crystalline compounds, containing water of crystallisation ; they are a little shifted to other wave-lengths and show other slight modifications, owing to the fact that the vibrating H_2O-group is not entirely free in the crystal, but must vibrate in the fields of force of the other constituents ; but there can be no doubt at all that the H_2O-group in all these cases is on the whole constant.

With the H_2O-group it is likewise possible to test Born's theorem with regard to the greatest possible number of vibrations : for Schaefer, Schubert, and Brieger found that the vibrations of the H_2O-group, which are simple ones in regular sulphates, are doubled in uni-axial and tripled in bi-axial sulphates, in fair accordance with the behaviour of the SO_4-vibrations themselves. The components of the doublets and triplets belong to the different axes of the crystal, as is shown by examination

[20] W. W. Coblentz, *Investig. of Infra-red Spectra,* Part III., p. 19, 1906 ; *Bull. Bur. of Stand.*, **7**, 619, 1912.

[21] Cl. Schaefer and M. Schubert, *Ann. Physik,* **50**, 339, 1916.

[22] K. Brieger, *Ann. Physik,* **57**, 287, 1918.

with polarised radiation. From this fact it follows at once that the H_2O group is an essential part of the crystal-lattice, the symmetry of which is adopted by the H_2O-group itself. The same result was arrived at two years later in a less convincing manner by Vegard and Schjelderup [23] with the aid of Röntgen-Rays.

XV.

In addition to the above discussed internal vibrations, the polyatomic crystals possess also "external" vibrations in the sense defined in Section X. These have been found by the method of residual rays, in most cases by Rubens and his collaborators.[24] Table III. gives the external fundamentals for some carbonates and two nitrates :—

TABLE III.

Substance.	External Frequencies.																
Siderite .	27μ		30			50		51									
Zincspar .			31	33	35			56									
Calcite .	28		30·3											94			
Dolomite .	27·5	29							68	74							
Aragonite .			34	36				50				85	88				100
Strontianite.						42	47										
Witherite .						45·5		56									
Cerussite .									64					94			
$NaNO_3$.						46											110
$PbNO_3$.										79							

Further Rubens has found by the same method the fundamentals shown in Table IV. with other polyatomic crystals :—

TABLE IV.

Substance.	Frequencies.	Method.
NH_4Cl . .	51·5μ	Residual Rays.
NH_4Br . .	59·3	,, ,,
$PbCl$ . .	91	,, ,,
$HgCl$ . .	95	,, ,,
Hg_2Cl_2 . .	98·8	,, ,,

As these external vibrations are vibrations of the crystal-lattice, they correspond to definite crystal-directions. The results are shown in Table V.

Reviewing the matter we must state the following :—

With prismatic resolution, it is possible to get all wave-lengths in a continuous manner from the visible to 22μ. Further progress is then only possible by using a diffraction grating of small dispersion ; in this way it is possible to attain all wave-lengths up to 40μ.[25] The accuracy

[23] L. Vegard and H. Schjelderup, *Ann. Physik*, **54**, 146, 1917.

[24] H. Liebisch and H. Rubens, *Ber.*, 198 and 876 (1919) ; 211 (1921).

[25] Recently M. Czerny (*Z. Physik*, **34**, 227, 1925) and R. M. Badger (*Proc. Nat. Acad. of Sci.*, **13**, 408, 1927), were able to extend this limit up to 130μ.

TABLE V.

Substance.		External Frequencies.
Siderite	*o*	30 51
	e	27 50
Zincspar	*o*	33 35
	e	31 56
Calcite	*o*	30·3 (55) 94
	e	28·0 94
Dolomite	*o*	29 74
	e	27·5 68
Aragonite	*r*	36 50 85
	b	36 50 100
	t	34 50 88
Witherite	*r*	56
	⊥ *r*	45·5
Cerussite	*r*	64 94
	b	64
	t	64
$NaNO_3$	*o*	46 110
	e	46 110

is not very great, on account of the small resolving power of the used grating. Beyond these wave-lengths, however, there we have only the approximately monochromatic wave-lengths of the residual rays, which are to be found in the above Tables.

Rubens and his collaborators, specially Liebisch, have investigated a great number of solid bodies throughout the whole spectrum, examining the reflectivity and the transmissivity from 1μ to 22μ with prismatic resolution, to 40μ with gratings, beyond these wave-lengths up to 300μ with residual rays. In this way one gets, of course, only a first survey on the behaviour of the crystal, but this is in many cases very useful.

In this way a great number of crystals were examined; the results cannot be reproduced here and we must refer the reader to the original papers.

XVI.

Before concluding this brief report, it may be worth while to discuss the question as to what lines of work would seem desirable in the future. It is obvious that such an attempt must have a yet more subjective character than the foregoing parts of this report.

We will restrict ourselves to the discussion of three problems.

(1) It seems reasonable to extend the investigations on the fundamentals of chemical radicals as far as possible. It will then be possible to trace conclusions on the configuration of these radicals. For instance, a thorough investigation of the fundamentals and the combinations of the SO_4-group would be highly desirable. Rolan [26] has investigated this group theoretically, but only very little has yet been done experiment-

[26] K. Rolan, *Z. Physik*, **39**, 588, 1926.

ally.[27] Things are, of course, more complicated for the SO_4-group than for the CO_3-group; for in regular sulphates the four O atoms lie at the corners of an equilateral tetrahedron, in the centre of gravity of which is situated the S atom. There seem to exist two active fundamentals, which can be identified with these found experimentally at 9μ and at 16μ; but there are also *inactive* fundamentals, about which nothing is known, either theoretically or experimentally.

(2) A question, which seems of great interest, is the ascertainment of the manner in which the absorption bands depend upon temperature. From the theoretical point of view it is to be expected that the combination-frequencies will disappear at very low temperatures; if this be true, they must show a much greater dependence on temperature than the fundamentals. Very little work has been done up to the present.[28] It seems desirable to remedy this deficiency, because many other questions (*e.g.* the conductivity of heat in crystals) seem to be connected with it.[29]

(3) The third problem, the thorough investigation of which I would propose, is the investigation of the connection between infra-red spectrum and the Raman effect. There are lines in the infra-red spectrum, which do not appear on the photographic plate in the Raman effect. And *vice versa :* there exist *inactive* fundamentals which are the strongest lines found by the Raman method. What is the cause of this different behaviour? I have ventured[30] to suggest the idea, that there might be a connection with the symmetrical or unsymmetrical type of the mechanical vibration (see the remarks at the end of Section III.), but there is too little experimental evidence to test this opinion. Among the numerous problems of the Raman effect this seems to me one of the most interesting : why do not all spectrum lines appear in Raman effect? And why, on the contrary, do such lines appear as do not manifest themselves in the spectrum? Some attempt in this direction has been made in my laboratory where we have investigated the Raman effect of NaCl, KCl, LiF, NaF, CaF_2 on the one hand (the active fundamentals do not appear in the Raman effect), and of the carbonates and $NaNO_3$ on the other hand (the inactive fundamental appears very strongly). Some experiments on the SO_4-group were also made. But nothing definite can be said at the moment, so that I can only express the wish that other experimenters should aid us in the elucidation of this problem.

[27] Cl. Schaefer and M. Thomas, *Z. Physik*, **12**, 330, 1923.

[28] H. Rubens and G. Hertz, *Ber.*, 256, 1912; O. Reinkober and H. Kipcke, *Z. Physik*, **48**, 205, 1928; P. P. Ewald, *Naturwiss.*, **10**, 1057, 1922.

[29] P. Debye *Wolfskehl Vorträge zu Gottingen* (Leipzig, 1914, Anhang, 46); A. Eucken, *Ann. Physik*, **34**, 185, 1911.

[30] Cl. Schaefer, *Z. Physik*, **54**, 153, 1929.

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INFRA-RED ABSORPTION SPECTRA OF SALTS CONTAINING THE GROUP AX_4.

By A. M. Taylor, *Professor of Physical Optics in the University of Rochester, N.Y., U.S.A.*

Received, 27th August, 1929.

Schaefer and Schubert [1] examined the reflection spectra of sulphates, chromates, and selenates, and Rolan [2] theoretically investigated the vibrations of the SO_4 group. He found that there should be two fundamental frequencies of vibration, and this agreed with Schaefer's measurement of the sulphates, where two maxima of reflection occur at 9μ and 16μ. For chromates and selenates, one maximum is found at $11{\cdot}16\mu$ and $11{\cdot}20\mu$ respectively; the second, which must be assumed to exist, is situated at wave-lengths greater than 20μ, the limit of Schaefer's measurement. It was felt that measurement of absorption spectra of different salts containing AX_4 groups would be useful, and it was with the object of connecting up the vibrations with the size and electrical constitution of the groups and of correlating the absorption spectra in the visible region with those in the infra-red, that this series of measurements was undertaken.

Experimental.

There were two factors influencing the choice of method. First, the difficulty of obtaining some of the salts to be examined, in large crystals which could be ground to sufficient thinness. Secondly, the difficulty which had been found in deciding which of the observed bands in a transmission spectrum were really due to absorption within the crystal slice, and which were spurious bands due to interference [3] between the beams reflected at two surfaces of the slice. For these reasons, a simple method described by Tolksdorf [4] was used with slight modifications. A plate of rock salt was polished on one side and left with a ground surface on the other. Into this latter surface the salt to be examined, previously finely powdered in an agate mortar, was rubbed with a smooth agate pestle. By this means, films of the salt of varying thickness and opacity could be prepared easily and quickly. Tolksdorf employed a very similar method, except that she then covered her film with a second plate of polished rock salt, and waxed the edges to exclude moisture. This made the film permanent, but it had the disadvantage that the two rock salt plates constitute a veritable Fabry and Pérot interferometer, and interference within the air film between the two plates causes bands to appear in the spectrum, unless the air film be very thin indeed, *i.e.*, less than the shortest wave-length of the radiation used. This being the case, it was necessary to give up the covering plate, and to use only the single plate with adhering film of the substance to be examined. This

[1] Schaefer and Schubert, *Ann. Physik*, **50**, 283, 1916; *Z. Physik*, **7**, 297, 1921.
[2] Rolan, *Z. Physik*, **39**, 588, 1926.
[3] A. M. Taylor, *Phil. Mag.*, **4**, 682, 1927; and *Phil. Mag.*, **6**, 88, 1928.
[4] Tolksdorf, *Z. physik. Chem.*, **132**, 161, 1928.

gave admirable results so long as a fresh plate was used each time. From day to day the plates could not be kept because of the effect, presently to be described, of moisture on the film. The rock salt plates were usually 1 mm. or more in thickness, so that interference bands from the plate itself were of no importance, as they would be too fine to be observed. A compensating plate (similarly ground on one surface, polished on the other, but naturally without the film of substance), was used in the air path. The film was irregular in nature, and usually excessively thin; these two factors combined to eliminate any trace of spurious bands due to interference, such as are obtained by the use of films of highly polished material of the order of 30μ or 40μ thick. The spectrum obtained could, therefore, be interpreted as a true absorption spectrum. The infra-red spectrometer was that described in earlier papers, and was used with a rock salt prism of 60°. The spectral region examined was 3μ to 14·5μ.

The four salts measured were the sulphate, chromate, perchlorate and permanganate. The potassium salts were chosen because they crystallised in anhydrous form, and were not deliquescent. In one case, the choice was unfortunate, because (as will be described), in the presence of moist air, double decomposition occurred on the surface of the rock salt plate and caused the formation of the sodium salt. For this reason it was necessary to make all measurements with freshly-prepared plates.

Results.

The curves, Figs. 1 to 4, show the general characteristics of the absorption spectra. The upper curves in each Figure are from comparatively thick films of substance (distinctly opaque to the eye); the lower are for very thin films (barely perceptible as a milky appearance or a faint coloration). The density of points of observation was about fifty per 1μ wave-length.

The curve for potassium chromate was peculiar in that a film several days old gave an additional band at 8·9μ, as indicated by the dotted line in Fig. 2. It was found that a freshly-prepared film only gave the band at 9·2μ, and that the production of the additional band could be accelerated by merely breathing on the film. A film of sodium chromate was then examined, and it was found to give only the band at 8·9μ, and none at 9·2μ. Clearly, in the presence of atmospheric moisture, the film of potassium chromate underwent double decomposition with the rock salt, producing a layer of mixed chromates. This explains the apparent anomaly.

Discussion.

The family likeness between the four curves is sufficiently striking. All four salts show a very intense absorption at positions not very far removed from 10μ. The reflection curves measured by Schaefer [1] show that the second characteristic frequency which lies at 16μ for sulphates and at wave-lengths greater than 20μ for chromates varies very greatly with the nature of the central atom of the AX_4 group.

This tetrahedral group is mechanically similar to methane CH_4, and like it, has two fundamental vibrations which are active in producing absorption bands in the spectrum. There should be a third—a symmetrical "breathing" of the whole group—but this being unaccompanied by alteration of electric moment, is inactive.

The frequency, which in all the salts occurs at about 9μ or 11μ, is due to the oscillation of the oxygen atoms which are common to all the groups; this oscillation is along the median of the tetrahedron. The other frequency is that of the oscillation of the central atom. Naturally, enough, this varies very greatly with the mass of the atom.

It will be easily understood that the vibrations of the oxygen atoms will not be much affected by the nature of the central atom; but it may

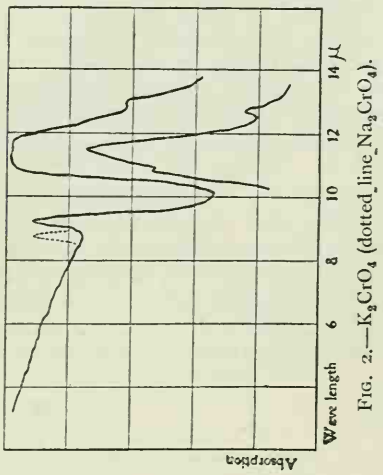

FIG. 2.—K_2CrO_4 (dotted line Na_2CrO_4).

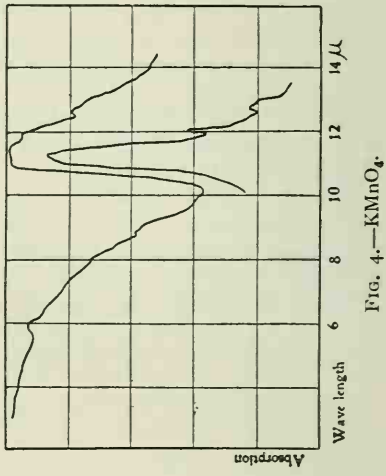

FIG. 4.—$KMnO_4$.

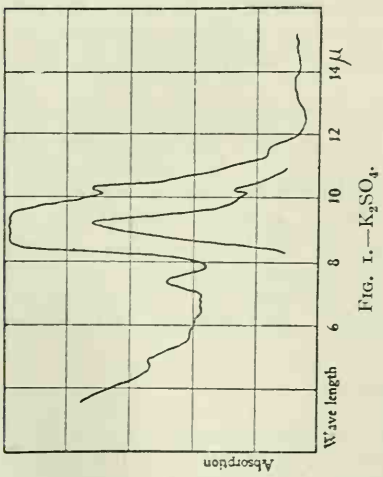

FIG. 1.—K_2SO_4.

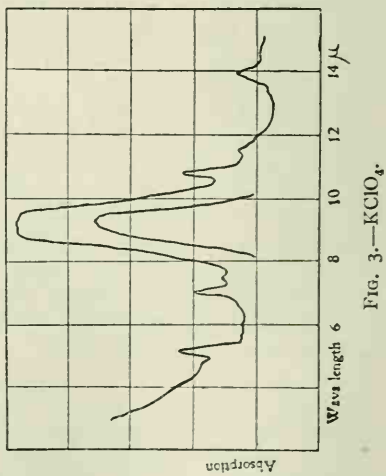

FIG. 3.—$KClO_4$.

be expected that the negatively charged oxygen atoms will oscillate more slowly as they become further removed from the positively charged central atom, *i.e.*, as the radius of the latter increases. At the same time, an increase of charge on the latter will tend to tighten up the group and cause the oxygen atoms to vibrate more rapidly. This is seen to be the case; sulphates and chromates, perchlorates and permanganates, exemplify the slowing down of the oscillation of the oxygen atoms as the group becomes larger, while the fact that permanganates and chromates

show bands at 11·25μ and 11·5μ respectively, shows that the effect of increased charge on the central ion is to tighten up the group.

The ascription of the frequency ν_2 is easily made, and also that of ν_1 when it happens to fall within the reigon of experimental measurement. The assigning of an origin to the other bands is by no means easy. The scheme indicated in the table is plausible, and though the numerical

TABLE.

Wave-numbers and Wave-lengths.

K_2SO_4.	K_2CrO_4.	$KClO_4$.	$KMnO_4$.	Origin.
625 cm.$^{-1}$* (16·0μ)	—	720 cm.$^{-1}$ (13·9μ)	—	ν_1
980 (10·2)	787 cm.$^{-1}$ (12·7μ)	930 (10·76)	833 cm.$^{-1}$ (12·0μ)	—
1092 (9·15)	870 (11·5)	1080 (9·25)	888 (11·25)	ν_2
—	1087 (9·2)	1430 (7·0)	788 (12·7)	$2\nu_1$
1370 (7·3)	—	—	—	$2\nu_2 - \nu_1$
2080 (4·8)	—	1960 (5·1)	1780 (5·8)	$2\nu_2$

agreement of the band frequency with the frequency which may be calculated from the origin suggested in the last column is poor, yet perhaps it is not straining belief in a "Kratzer correction" applied to overtones to suggest that this might account for the discrepancies. The serious defect in the scheme is that $2\nu_1$ for chromates is made to appear at 9·2μ, where there is a strong band, yet ν_1 was certainly not found by Schaefer, who examined the reflection spectra up to 20μ. There is also the fact that for permanganates the band at 12·7μ which is ascribed to $2\nu_1$ is that which corresponds to the frequency difference 795 found in the visible spectrum.[5] It might have been expected that this frequency would have been found to be the *fundamental* vibration of the Mn atom within the group. Judging from the weak intensity of the band at 12·7μ in the infra-red spectrum, it is not a fundamental; it is ascribed in the table to the first harmonic $2\nu_1$. This seems peculiar, and suggestions would be very welcome.

There is in every case a small band, separated by a distance of the order of 100 wave-numbers from the band ν_2, on the long wave-length side of it. This may possibly be due to the dichroism noticed by Schaefer. It would hardly be expected that the AX_4 group should be symmetrical. The small birefringence in the optical region shows that it has a slight but definite distortion.

This work on the AX_4 groups is by no means complete, and comparison with other salts would possibly throw much light upon the problems.

* Schaefer's measurements by reflection.

[5] A. M. Taylor, paper contributed to this discussion, see p. 861.

Information in the region between the visible spectrum and 3μ would be valuable.

My thanks are due particularly to the Ramsay Memorial Fellowship Trustees, by whose kindness I have been enabled to pursue these investigations; and also to Professor T. M. Lowry, F.R.S., and to Dr. E. K. Rideal for their continued interest.

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THE BAND SPECTRUM OF $KMnO_4$ IN THE CRYSTALLINE STATE AND IN SOLUTION.

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Received 7th August, 1929.

In a paper last year, Joos[1] suggested an explanation of the bands observed in the visible region of the spectrum when light transmitted through certain coloured crystals was analysed by a spectroscope. The suggestion put forward is a perfectly general one, and is well known to spectroscopists. It is that the frequency of any particular line can, in general, be expressed as a sum of terms which themselves are fundamentals, characteristic of energy states of definite units in the crystal lattice. This may be symbolised

$$\nu = \Sigma(n_1\nu_1 + n_2\nu_2 + \text{etc.}),$$

where n_1, n_2, etc., are integers, and ν is the frequency of the line.

In the most general case a crystal possesses three different types of fundamental. The first is due to electronic transitions within individual atoms; the second to vibrations of the atoms within chemical or crystallographic groups; the third to vibrations of atoms or groups about their mean positions in the crystal lattice. As an example of these, we may consider copper sulphate. Here there is the blue colour of the copper ion, the fundamental frequencies of vibration of the SO_4 group and the long wave-length *Reststrahlen* frequency of vibration of the whole crystal lattice.

Now, in this case, the blue colour of the crystal is associated with the hydrated copper ion, but the characteristic frequencies of the second type are due to the internal vibrations of the SO_4 group, and there is no coupling between these two terms. That is to say, we should not expect these two types to combine together to give a banded spectrum. Vibrations of the Cu ion within its co-ordinated environment of water molecules should certainly combine with the electronic term, though such combination has not been observed in the visible spectrum. Terms which would be likely to combine would be the internal vibration of the SO_4 group with the electronic terms of the sulphur or oxygen atoms. These bands, if they occur, will be in the ultra-violet; we are only considering the visible region.

The MnO_4 group is coloured, and moreover its colour varies with the

[1] Joos, *Physik. Z.*, **29**, 117, 1928.

state of oxidation of the Mn atom, *i.e.*, with its electric charge: MnO_4^- is purple, and MnO_4^{--} is green. The electronic transitions responsible for the colour are therefore those between different states of the Mn atom. The manganese ion is always coloured in whatever state it is found, and it is hardly to be thought that the oxygen ions which elsewhere are colourless are contributing to the colour.

It is legitimate to assume a similar structure for the MnO_4 and SO_4 groups, since barium sulphate and potassium permanganate are crystallographically similar. Therefore, the Mn ion which absorbs light is itself capable of oscillation with a definite frequency ν_2 within the tetrahedron of oxygen atoms surrounding it. If the frequency corresponding to the electronic transition be ν_1, the frequency of the light absorbed by the Mn ion will be given by

$$\nu = \nu_1 + n_2\nu_2 + n_3\nu_3.$$

The term ν_3 is the frequency of oscillation of the whole MnO_4 group within the crystal lattice. This is small, and will probably only cause a blurring of the bands $\nu = \nu_1 + n_2\nu_2$. A further cause of blurring will be that the vibration ν_4 of the oxygen atoms of the MnO_4 group is coupled with that of the manganese atom and so the possibility of a further weak fine structure is introduced.

Crystalline Permanganate.

A photograph of the absorption spectrum of $KMnO_4$ is shown in Fig. 1, which will be found facing page 829.

This was obtained by grinding $KMnO_4$ to a fine powder in an agate mortar, and then rubbing the powder between two pieces of finely-ground glass. On separating the pieces of glass, a uniform purple film was obtained of sufficient transparency to give a good spectrum by transmitted light.

It is seen from the Fig. that a band spectrum is obtained, and that the bands are equidistant. The wave-lengths were measured up by comparison with an iron arc spectrum, and the frequencies of the long wave-length side of the bands are given in Table I. :—

TABLE I.

Band.	Wave-length in Å.	Wave-number in cms. $^{-1}$	Difference of Wave-number.
I.	5776	17,313	
			787
II.	5525	18,100	
			821
III.	5285	18,921	
			803
IV.	5070	19,724	
			810
V.	4870	20,534	
			783
VI.	4691	21,317	
			783
VII.	4525	22,100	
			794
VIII.	4368	22,894	

Mean wave-number difference = 797 cms. $^{-1}$.

The wave-number of any band may be expressed as $\nu = \nu_1 + n\nu_2$ where $\nu_1 = 17{,}313$ and $\nu_2 = 797$. Comparison of the size of $h\nu_2$ with the average energy kT present in each degree of freedom of the crystal shows that there are too few groups at ordinary temperatures in the

first vibrational state, for there to be any great intensity of absorption corresponding to $\nu_1 - \nu_2$.

The bands are broad and fuzzy, and the reasons for this have already been mentioned; there is also the additional effect of mutual interference of neighbouring atoms. This, by cutting short the resonance, causes a broadening of the width of any absorption line, according to the usual Fourier analysis. The fact that the bands are observed at all seems to be peculiar, as neither manganates nor chromates which contain similarly constituted coloured groups show spectra in which bands can be detected, a most disappointing state of affairs.

The absorption spectrum of $KMnO_4$ in the infra-red was determined, and a band found at $12{\cdot}7\mu$, *i.e.*, at a wave-number of 788. This frequency agrees well with ν_2 already found from the visible spectrum; it is, in fact, the frequency of vibration of the Mn atom within the tetrahedron of oxygen atoms. The infra-red spectrum was obtained by passing radiation through a film of permanganate prepared by rubbing the finely-powdered material with an agate pestle on to the ground surface of a rock salt plate. The other surface of the rock salt plate was polished.

Aqueous Solution of Permanganate.

A very interesting effect is observed in the band spectrum of permanganate, on dissolving the salt in water. The bands are now less widely spaced than before, the frequency difference being only 744 wave-numbers. This clearly shows the slowing down of the rate of vibration of the Mn atom within the MnO_4 group. That is to say, the negatively-charged group becomes surrounded with an "atmosphere" of oriented water molecules, and the reaction of these polar molecules upon the group is to pull it somewhat apart. The dipoles of the water molecules are so oriented that their field is one of attraction for the negatively-charged oxygen atoms, and this loosens the binding of the group. As a result, the frequency of vibration is diminished. It is noticeable that the effect of the surrounding atmosphere of oriented water molecules is greater than the effect of the K^+ ions which surround the MnO_4^- ion in the crystal. Table II. gives the wave-lengths of the bands observed in the spectrum of an aqueous solution of $KMnO_4$. Fig. 1(*b*) is a photograph of the spectrum.

TABLE II.

Band.	Wave-length in Å.	Wave-number in cms.$^{-1}$	Wave-number Difference.
I.	5770	17,331	
			759
II.	5528	18,090	
			742
III.	5310	18,832	
			737
IV.	5110	19,569	
			760
V.	4919	20,329	
			724
VI.	4750	21,053	

Mean wave-number difference 744 cms.$^{-1}$.

Non-Electrolytic Solutions.

As a check upon this explanation, a solution of $KMnO_4$ was prepared in a solvent of lower dielectric constant than water, and its absorption

spectrum photographed. Ethyl acetate was carefully dried by standing first over freshly-fused calcium chloride, and then over phosphorous pentoxide. It was distilled with a long fractionating column, and the distillate was collected at 77·1° C. It had a specific resistance of 3·74 megohms, so that its dryness was unquestionable. In this solvent, $KMnO_4$ (previously finely powdered and stood in a vacuum dessicator over phosphorous pentoxide for some days) was dissolved; the solution saturated at 18° C. was $0{\cdot}7 \times 10^{-3}$ molar. The solution had a specific resistance of 2·51 megohms, so that the molecular conductivity of the solute was 1·13 units.[2] The sum of the mobilities of K^+ and MnO_4^- ions in ethyl acetate, calculated from their mobilities in water by means of a viscosity correction, is about 70 at 18° C. The ionisation of the solute was therefore about 1·6 per cent.

The absorption spectrum of this solution is very similar to that of crystalline potassium permanganate. The wave-lengths of the bands are given in Table III. and the average spacing is now 785 wave-numbers, or almost that found for the spacing in the spectrum of the solid.

TABLE III.

Band.	Wave-length in Å.	Wave-number in cms. $^{-1}$	Wave-number Difference.
I.	5763	17,352	
			797
II.	5510	18,149	
			762
III.	5288	18,911	
			813
IV.	5070	19,724	
			768
V.	4880	20,492	

Mean wave-number difference 785 cms. $^{-1}$.

This supports the view that the alteration in band spacing in aqueous solution is due to the hydration of the MnO_4^- ions. Ethyl acetate, a solvent of dielectric constant 6, does not exert sufficient influence on the molecule of potassium permanganate to cause it to dissociate, nor does it alter appreciably the rate of vibration of the Mn atom. Water, a solvent of dielectric constant 80, ionises the molecule, and provides an atmosphere of oriented dipoles which gives rise to a field strong enough to loosen the constraints within the MnO_4^- group, thereby causing the Mn atom to oscillate more slowly.

Summary.

Reasons are given for expecting that the absorption spectrum of potassium permanganate in the visible region should be banded. Such a band spectrum is found and the frequency difference between the bands is the frequency of oscillation of the Mn atom as determined from the infra-red spectrum of $KMnO_4$. The spectra of permanganate in the crystalline state, in aqueous and in ethyl acetate solution, are photographed and compared. Differences in band spacing are attributed to the influence of solvation upon the MnO_4^- ion.

The Laboratory of Physical Chemistry,
Cambridge, England.

[2] I wish to thank Dr. F. L. Gilbert of Cambridge, by whose kindness I was enabled to make these measurements.

PART III (b) INTRODUCTORY PAPER—THE INFRA-RED SPECTRA OF LIQUIDS.

By Jean Lecomte (*Docteur ès Sciences, Laboratoire des Recherches Physique, Sorbonne*).

Received in French, 24th June, 1929, and translated by F. L. Jones, B.A

Considerations of space only permit an outline of a very complex subject: after a short history of the subject, it is proposed: (I.) to give an account of some experimental results on the infra-red spectra of liquids (absorption, reflection, and magnetic rotation spectra); then (II.) to summarise the general results obtained (the description of chemical properties and the study of the constitution of substances); passing on (III.) to calculations on these spectra. Then we shall try (IV.) to define the position which the infra-red spectra of liquids holds in physics. Finally (V.) we shall consider some of the principal problems that remain unsolved in the infra-red.

Historically, the knowledge of the infra-red spectra of liquids increased with the progressive extensions towards longer wave-lengths. At the time of Langley (1880) they were limited to wave-lengths of a few microns. Afterwards came the researches of Rubens and Paschen, who pushed on from $9{\cdot}4\mu$ to almost 18μ. The discovery of residual rays by Rubens and Nichols (1897) enabled 152μ to be reached, and by focal separation with quartz lenses Rubens and Wood (1910) went beyond 300μ. The recent work of Nichols and Tear (1924) has laid bare for investigation the remaining portion of electro-magnetic rays (300μ to 2 mm.).

It should be mentioned, before proceeding further, that although numerous researches have been directed to the study of liquids in those parts of the spectrum successively opened for research and although a truly imposing number of papers has accumulated on the subject, the main question is, nevertheless, still only in its infancy. In the infra-red spectra of solids, and especially of gases, more or less definite results have been obtained, as much from a theoretical as from an experimental standpoint, yet the gaps that occur in the study of liquids seriously impede the development of theories on the subject taken as a whole.

I. An Account of some Experimental Results on the Infra-red Spectra of Liquids.

(A) *Absorption Spectra.*—As a matter of fact, the greatest number of results concern absorption spectra. Indeed, from the point of view of technique, their study is one of the least difficult in the whole of the infra-red, because it is sufficient to place a cell of the liquid of appropriate thickness in front of the slit of a monochromator or of a spectrometer. Nothing could be easier than to vary the thickness of the cell, while in the case of solids, for example, it is almost impossible to get plates of the substance sufficiently thin.

As examples, we will choose the results obtained with pure liquids, *e.g.*, water and the aliphatic hydrocarbons, following those with some results on aqueous solutions.

Water.—This is one of the liquids most opaque to the infra red : so much so that for rays above 3μ it is necessary to use layers of only a few microns thick. Rubens and Ladenburg [1] in order to reach 18μ, used an extremely thin film of slightly soapy water on a sort of horseshoe. It is found that a layer of water 1 cm. thick stops all rays above $1{\cdot}4\mu$.

Authorities agree that the principal bands of water are about $1{\cdot}5$, 2, 3, $4{\cdot}7$, and 6μ. Beyond this the extinction coefficient apparently increases, approximately uniformly, reaching 0·428 at 18μ (Rubens and Ladenburg). Aschkinass [2] gives the value of the absorption coefficient to about $8{\cdot}5\mu$. Tamman [3] occupies himself with the band at $4{\cdot}7\mu$. Grantham,[4] Collins,[5] Ellis,[6] and Dreisch [7] were concerned with obtaining greater dispersion ; they determined very accurately the position and coefficients of absorption of the bands, but did not discover any new results. In the longer wave-lengths, the residual rays of NaCl(52μ), KCl(63μ), and KBr(83μ) are completely absorbed by 1 mm. of water ; 33 per cent of the rays from a quartz mercury lamp isolated by the method of quartz lenses (about 300μ) are absorbed by 0·038 mm. of water (39·8 per cent. and 38·4 per cent. respectively, if these rays are first filtered by 0·038 mm. of black cardboard or 2 mm. of quartz (Rubens)).

Saturated Aliphatic Hydrocarbons.—Ellis [6] worked up to $2{\cdot}7\mu$, using thicknesses of 1 cm. and over; V. Henri [8] and Marton,[9] up to about 5μ, with thickness between 0·02 and 10 mm. ; Coblentz [10] from $2{\cdot}5$ to 14μ, and J. Lecomte [11] from $2{\cdot}5$ to 16μ, used cells 0·01 to 0·2 mm. One of the latest workers, Fullweiler,[12] has gone up to $0{\cdot}9\mu$ photographically. It is extremely remarkable, when passing from member to member of a series, for example, from hexane to duodecane (for we are limited to liquid hydrocarbons), to find that the *principal* regions of absorption are in approximately the same part of the spectrum, with intensities of the same order of magnitude. This truly remarkable regularity often noticed in the original memoirs, is not fortuitous, and is the starting-point of many of the theoretical considerations developed later in this paper. Near the visible spectrum are found absorption maxima of increasing intensities at $0{\cdot}9$, $1{\cdot}02$, $1{\cdot}117$, $1{\cdot}38$, $1{\cdot}71$, $2{\cdot}17\mu$, then very strong bands are met at $3{\cdot}43$, $6{\cdot}86$, and $13{\cdot}6$ to 14μ. Nevertheless, the spectra of the saturated aliphatic hydrocarbons are not absolutely identical, because many feeble bands appear in the spectra of individual hydrocarbons, which appear to be a property of these individuals. Fig. 1, from the work of Ellis, and Fig. 2, from personal measurements, give the general run of the transmission spectra of hydrocarbons in the near and middle infra-red.

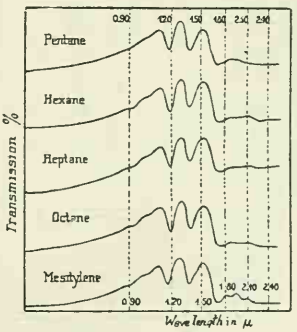

Fig. 1.—Transmission of Hydrocarbons.

Aqueous Solutions.—We find here a very curious phenomenon. When salts which easily form hydrates, such as $CaCl_2$, $Al_2(SO_4)_3$, are dissolved in water, the solution may be more transparent in certain parts of the infra-red spectrum. Various explanations have been advanced to account for this phenomenon. According to the solvate theory, the dissolved salts form slightly stable compounds with the water which are more transparent to the infra-red than water under the same conditions.

According to other authors, there exist in water several kinds of molecules which possess different absorption bands. Unfortunately, neither one nor the other of these interesting hypotheses accounts for all the results observed.

The object of the researches of the school of Schaefer, Paulus, Jones, etc., was to find support for the theory of solvates by determining, up to about 1·3μ, the absorption spectra of strongly hydrated salts. Grantham,[4] and more recently Collins,[5] have investigated the influence of the addition of alkaline hydroxides, and many other substances, on the spectrum of water up to about a maximum wave-length of 3μ. They found that dissolution causes an increase in certain of the water absorption bands and a decrease in others.

In general, the great difficulty in the study of solutions (aqueous or otherwise) is the large infra-red absorption of all known solvents. Often

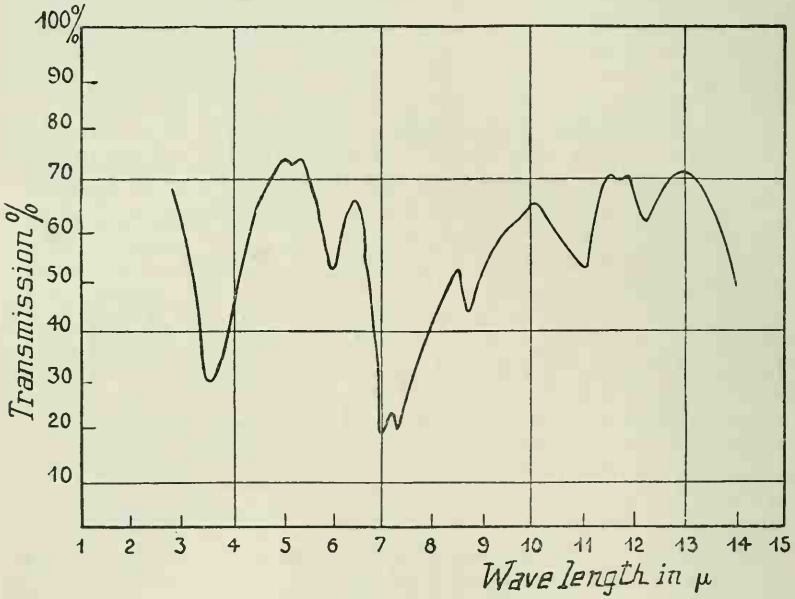

FIG. 2.—Transmission of Diisoamylene.

the presence of the solvent produces big opaque regions which prevent the drawing of precise conclusions from the measurements.

(B) *Reflection Spectra.*—The reflection spectra of liquids in the infra-red are much less accurately known than those of solids on the one hand, and than their own absorption spectra on the other; this is due to the fact that their reflecting powers are feeble and vary very little. Thus, several successive reflections do not give rise to a phenomenon similar to that of residual rays; there are in this case certain special conditions which make the study very difficult.

In a general way, reflection spectra of liquids follow the general characteristics of absorption spectra. Thus, Rubens and Ladenburg[1] observed, for water, reflection maxima near 3·2, 6·3 and 19·5μ, and minima near 2·7, 5·2 and 11·0μ, as could have been foreseen from the study of transmission spectra. The observations of these authors on ethyl alcohol result in similar conclusions. In the more remote

spectrum, up to about 300μ, the reflecting power of the liquids they have examined only varies slightly with wave-length, giving feeble maxima and poorly defined minima.

The studies of Pfund[13] on the aqueous solutions of sulphuric acid are very interesting (Fig. 3). Curve (I) (fuming sulphuric acid density 1·87) gives maxima at 7·20, 8·65, and 10·30μ. Curve (II.) (12 parts acid to 1 part water); and Curve (III.) (12 parts acid to 2·4 parts water), show that the maximum at 7·20μ has disappeared. With 3 parts acid to 1 part water, new maxima appear at 9·60μ and 8·40μ (Curve IV.). Curve (V.) (1 part H_2SO_4 to 1 part water) and Curve (VI.) (1 part acid to 3 parts water), and Curve (VII.) pure water complete the work.

(C) *Magnetic Rotatory Polarisation.*—We know that the Faraday effect decreases rapidly with increasing wave-length. Moreover, to obtain a measurable effect it is necessary to use layers of liquid of the order of 1 cm.; this causes the cell to be opaque, except to wave-lengths of a few microns. Up to the present these two reasons amongst others, have considerably limited the field of investigation. A possible method of minimising the difficulty would be to work with a very thin layer of liquid and a very intense field.

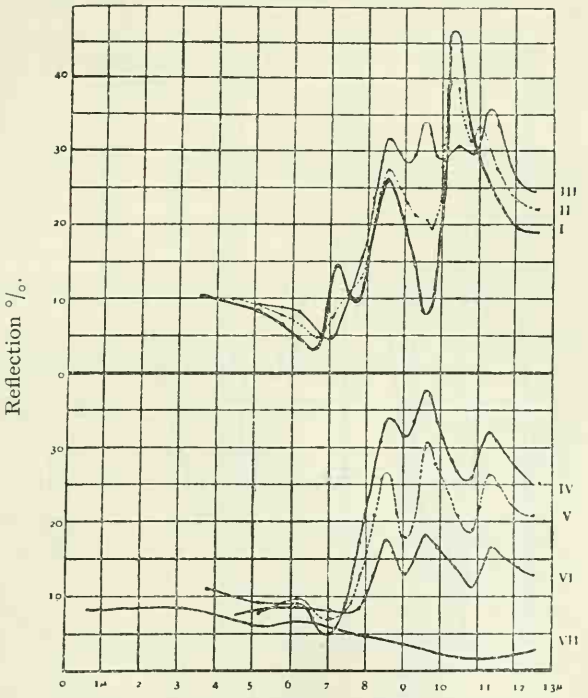

FIG. 3.—Reflection Spectra of Sulphuric Acid.

The results on carbon disulphide, examined by Moreau up to about 1·42μ, and then by Ingersoll[14] to 4·30μ, are in agreement with theoretically deduced formulæ. The theoretical formulæ of Drude account for several experimental results, and it would be interesting to investigate whether the "characteristic wave-lengths" which enter into his formulæ bear a relation to the infra-red bands actually found. In the case of CS_2 results are in good agreement with theory. The other researches of Ingersoll, on a certain number of liquids, unfortunately stop at about 2·3μ, that is to say, before the region of intense absorption bands, and so do not establish whether the bands have an influence on the magnetic rotation.

II. General Results on the Spectra of Liquids.

In the case of liquids, as with solids, it is possible to find *a correlation between their infra-red spectra and their chemical constitution.* This im-

portant result is due to the researches of Abney and Festing (1881), and nothing has been found since to disprove it.

Take, for example, the series of primary saturated aliphatic alcohols studied by Weniger[15] to about 13μ and our own up to about 15μ. In the near infra-red many researches can be referred to; among the most recent are those of Sappenfield,[16] and Smith and Boord.[17] The spectra of the *primary* alcohols, *i.e.*, those which contain a CH_2OH group, are very similar up to about 10μ, both in the position and in the intensity of the principal bands. Thus, in a survey of a homologous series, *e.g.*, the primary alcohols (methyl to octyl alcohol), or better still, a comparison of two isomers (*e.g.*, butyl and iso-butyl alcohol), the only differences between the members are a few feeble bands; on the other hand, beyond 10μ, all these spectra are distinguished one from the other. If, now, we

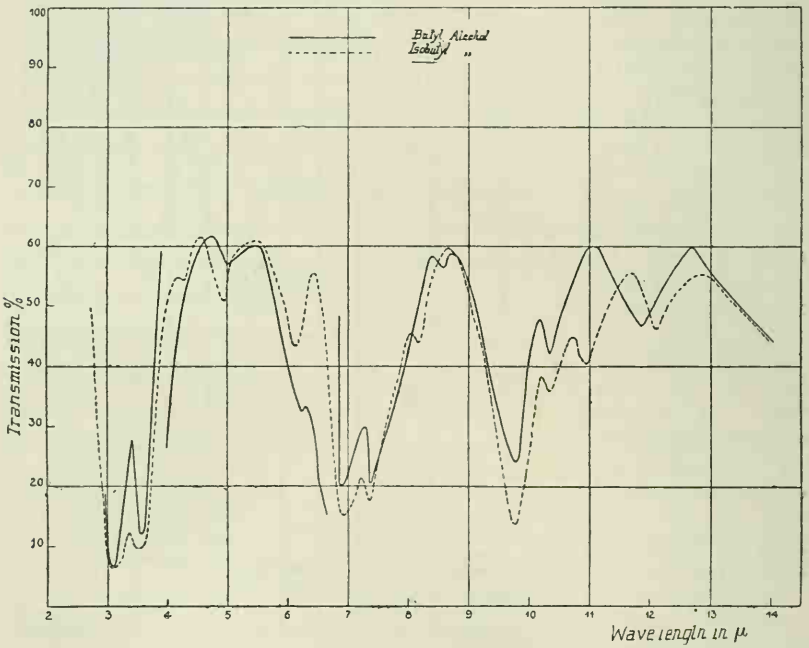

FIG. 4.—Transmission of Butyl and Iso-butyl Alcohol.

pass on to the *secondary* alcohols, that is to say, those characterised by CHOH groups or to the *tertiary* alcohols which are characterised by COH groups, we observe a complete change in the positions of the bands below 10μ, the most remarkable being the band which is at 9·7μ in primary alcohols, 9·1μ in secondary, and 8·5μ in tertiary alcohols.

Figs. 4, 5, and 6 are the results of the author's work, and are reprinted from his book, "Le Spectre Infra-rouge." They are, as a whole, in agreement with the measurements of Weniger. In determining the transmission curves of butyl and iso-butyl alcohols (Fig. 4), both primary-alcohols, the following thicknesses were used: in the former case 0·014 mm. from 3 to 4μ, and from 7μ to 14μ and 0·10 mm. below these wave-lengths; for the whole spectrum of iso-butyl alcohol, a thickness of 0·014 mm. The spectra of secondary butanol (Fig. 5), and of tertiary butyl alcohol (Fig. 6) were both determined with 0·014 mm. of

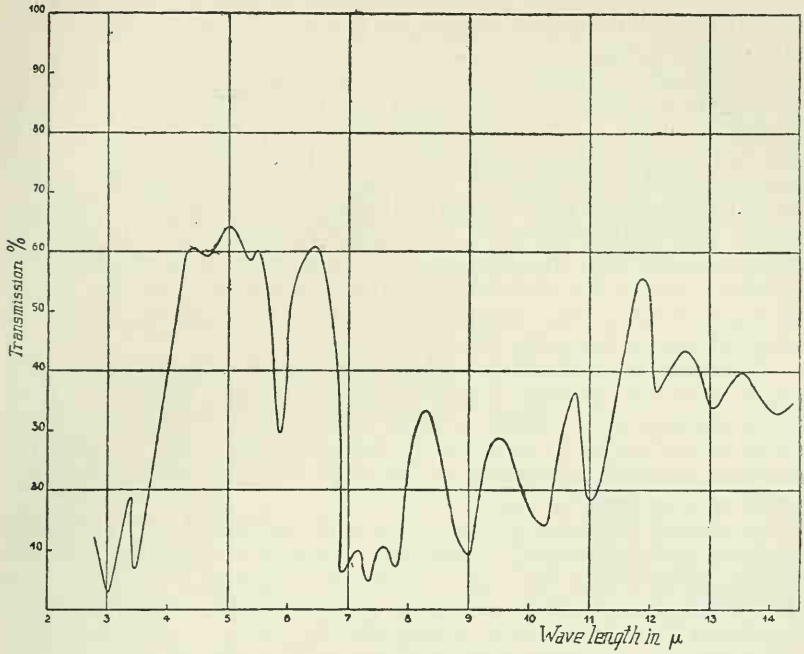

FIG. 5.—Transmission of Secondary Butyl Alcohol.

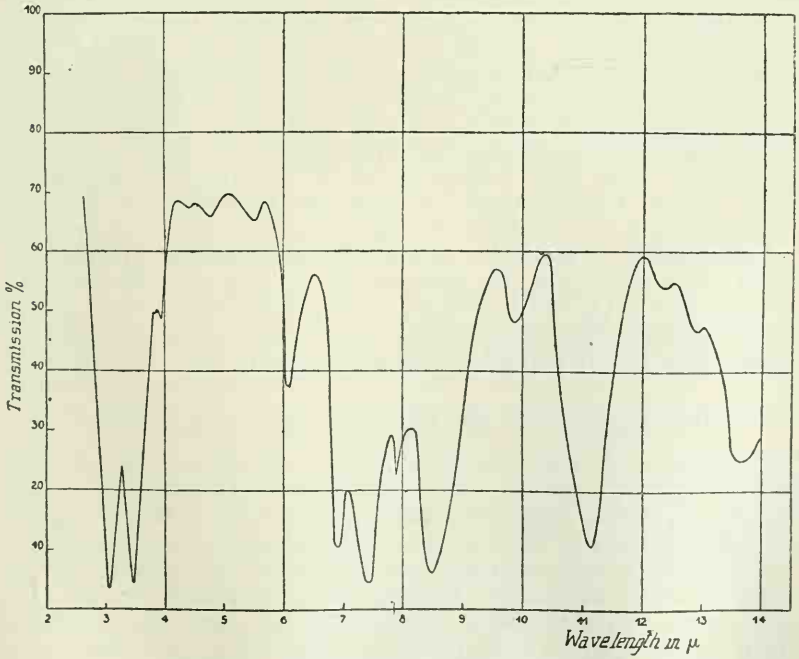

FIG. 6.—Transmission of Tertiary Butyl Alcohol.

liquid. A glance at these figures shows marked differences between the curves ; similar differences, though not so marked, are found in the near infra-red up to $2{\cdot}5\mu$.

Equally characteristic are the infra-red spectra of other series of compounds in organic chemistry. Thus, I have found that aliphatic ketones [11] possess a very strong band near $5{\cdot}9\mu$; the aromatic ketones give two equally intense bands, but at a little longer wave-length. According to Bell,[18] and Salant,[19] the primary amines (*e.g.*, aniline) have a strong band between 2·9 and 3μ, with the secondary amines (*e.g.*, diphenylamine), this band becomes less intense and disappears entirely with the tertiary amines (*e.g.*, triphenylamines). Other compounds having characteristic spectra are the aldehydes, the isomeric ketones, the esters, the isomeric acids, etc. Equally clear results have also been observed with carbonates,[18] nitrates, etc.

Conversely, it should be possible to determine the structure of a compound from a knowledge of its infra-red spectrum. One of the most recent researches on organic compounds is that by Ross,[20] who determined the infra-red spectrum of pyrone and found that its infra-red spectrum appeared to indicate the presence of a benzenoid group, and probably a hydroxyl group.

In mineral chemistry the most interesting problem investigated concerns the water contained in minerals. There is a distinction between "water of crystallisation" and "water of constitution." In the case of water of crystallisation, as in, *e.g.*, gypsum ($CaSO_4 . 2H_2O$), Coblentz has shown that the principal water bands are found in the spectrum of this substance. In other substances the water bands are superimposed on the characteristic bands of the compound, which they may completely mask. Schaefer and Schubert have concluded that the occluded water behaves as though it were itself anisotropic in an anisotropic crystal, uniaxial in an uniaxial crystal, and biaxial in a biaxial crystal. If, on the other hand, we consider "water of *constitution*" (*e.g.*, manganite $Mn(OH)_2$ and göthite $Fe(OH)_2$), all the water bands disappear except that at 3μ. It is well known that substances containing water of crystallisation lose their water progressively at various temperatures, while those that contain water of "constitution" decompose before any of it is given off. It would be interesting to find out whether there is a correlation between the intensity of the water bands and the number of molecules of water of crystallisation in the compound ; also whether all the molecules of water of crystallisation play the same part. Up to the present, these points have not been cleared up, principally because of the milky appearance crystals take on when submitted to dehydration whether partial or total.

III. Calculation of the Infra-Red Spectra of Liquids.

The first problem that arises is : What is the origin of the infra-red bands of liquids ? The solution is still remote, but we will indicate the methods at present employed in the hope of solving it. As all organic compounds containing carbon and hydrogen present a certain number of intense bands at approximately the same place, these bands can be attributed to the groups CH_3, CH_2, CH, or in accordance with the most recent views to the reciprocal vibrations of the carbon and hydrogen atoms ; in other words, to the bonds C—C and C—H. In a similar way, it is possible to recognise the vibrations C—Cl, C—Br, C—I, and N—H,

etc. In the case of the more complex groups (for example, the liquid carbonates), their bands are due to the vibrations of the CO_3 group. These *vibration spectra* are found in the near infra-red at wave-lengths rarely exceeding 14μ. In conformity with the results on solids and gases one is led to consider the movements of the molecule as a whole, as well as its internal vibrations. These are the *rotation spectra* situated at fairly long wave-lengths, which, in the case of liquids, do not appear to be found below 8 to 10μ. There is thus a zone where both rotation and vibration spectra are to be found. There are many papers on the vibration spectra and on the rotation-vibration spectra, but the pure rotation spectra of liquids, which are not easily obtained, are at present almost wholly unknown.

These hypotheses, even though they do not correspond exactly with all the facts, have, nevertheless, the advantage of accounting fairly well for certain of them. Thus, for example, they explain, firstly, why compounds possessing the same groups should give rise to approximately the same bands and such as are actually found. Then they permit one to see why compounds furthest removed in a homologous series, such as hexane and duodecane on the one hand, or methyl and octyl alcohols on the other, give rise to characteristic "vibration" bands having comparable intensities. Finally, since in passing from member to member of a homologous series the moments of inertia of the members vary, these hypotheses predict that each should have a different "rotation" spectrum. This is why the primary alcohols possess dissimilar spectra above 10μ, and why isomers like butyl and iso-butyl alcohol also differ above 10μ.

We shall now see how, as a consequence of these investigations, attempts have been made to *calculate* the spectra. The first idea, so far as it concerns vibrations alone, has consisted in examining series of bands forming harmonic series. Coblentz remarked some twenty years ago that the hydrocarbon bands at 1·71, 3·43, 6·86, 13·6-14μ sensibly fulfilled this condition. Later, according to the work of Kratzer on the spectra of gases, a correction has to be applied to the strictly harmonic relation. The frequency ν of the successive bands is related to the frequency ν_0 of the fundamental band, by a series of whole numbers n and a small constant x

$$\nu = \nu_0 n(1 - nx),$$

which gives a parabolic equation

$$\nu = An - Bn^2 \qquad \text{(A and B constants)}.$$

Very remarkable results on the infra-red spectra of liquids have been obtained by this conception, especially by Ellis,[9] Marton,[9] etc. . . . They have been able to calculate the constants of the Kratzer formula for the bonds C—C, C—H, C—Cl, . . . for a whole series of organic compounds, with good correlation between calculation and experiment.

We have been induced to inquire whether, as is the case with gases, there would not be, for liquids also, a succession of combination frequencies, since the preceding series does not explain all the bands measured. If $\nu_1, \nu_2, \nu_3 \ldots$ are the frequencies found by the above method of calculation, there will also be absorption at the frequency ν where

$$\nu = \nu_1 p_1 + \nu_2 p_2 + \nu_3 p_3 \ldots$$

and $p_1, p_2, p_3 \ldots$ are whole numbers, either positive or negative. This relation accounts for the observed bands, particularly in the case of benzenoid and aliphatic hydrocarbons.

We do not lose sight of the fact that a certain amount of criticism, very plausible in appearance, has been raised against this method of procedure. Thus, it would appear in the first place, that the higher harmonics should not possess a sufficient intensity to give rise to measurable bands. It is also objected that the choice of the fundamental ν_0 is arbitrary, and lastly that the determination of the infra-red spectra of liquids is still too crude to justify the application of the Kratzer correction. Combination frequencies should, on their part, permit of the prediction of the relative intensities of the different bands by mere inspection of the relative values of the constants p_1, p_2, p_3, etc. In many cases this prediction is not verified. Nevertheless, it seems to us that, pending fuller investigation, the harmonic relation, whether actual or approximate, will still render a great service to the calculation of infra-red spectra of liquids.

Among the other attempts at co-ordination, we may mention V. Henri's [8] application of the Ketteler-Helmholtz dispersion formula to the infra-red absorption coefficients of liquids. It is our opinion that the results obtained should induce workers to make a wider application to the more recent measurements of the ideas developed in the photochemical studies. On the other hand, Bonino, in the *Gaz. Chem. Ital.*, has brought forward a very interesting contribution to the theory of the infra-red spectra of liquids by incorporating the Bohr-Sommerfeld conditions. Owing to lack of space, it is necessary to refer the reader to the original literature, where the author also gives some account of the maximum molecular absorption coefficient.

We shall conclude with the work of Gapon,[21] who concerned himself chiefly with the relation

$$\nu = \nu'\sqrt{n}$$

where ν = the frequency of an observed band, ν' is a characteristic quantity similar to a frequency, and n is a whole number. He commences by determining ν' from the band which is supposed to correspond to $n = 1$. (This is one of the unsatisfactory points in his reasoning.) Using this value of ν', there is a satisfactory correlation between the calculated values of ν and the observed values. This is the method he employs to determine ν' empirically. Proceeding further with his analysis, he deduced a formula from which ν' can be calculated as a function of the molecular weight M, the molecular volume V, and the coefficient of compressibility β, with a constant K. The relation is:

$$\nu' = K\sqrt{\frac{V^{\frac{1}{3}}}{M\beta}}.$$

IV. The Physical Position of Infra-red Studies on Liquids.

The Connection with the Visible and the Ultra-Violet.—Infra-red spectra are connected in a direct way with the corresponding visible and ultra-violet spectra. Several authors have made good attempts at co-ordinating these spectra. According to V. Henri,[8] the frequencies of the ultra-violet bands are exact multiples of infra-red bands. He gives a number of important examples; but, since the multiples appear to be in the region of 40 to 50, they are completely arbitrary. Nevertheless, this hypothesis has an important connection with the quantum theory. Very important results of a similar nature have been given by Baly.[22]

According to his ideas, we can calculate the infra-red spectra from the ultra-violet, and *vice versa*. For example, in the case of each ultra-violet band there is determined the difference in frequency between each of its lines and its central line; this difference will give the frequency of the corresponding infra-red line. The converse procedure renders it possible to determine the ultra-violet bands from the infra-red. In practice, the results are reasonably satisfactory. In the case of benzene, for example, from an entirely personal conception of molecular frequencies and their associated atomic frequencies, Baly would explain, on the one hand, the position of the infra-red bands of liquids and their relative intensities, and on the other hand, he would obtain the frequencies of the central lines in the ultra-violet bands. Unfortunately, these deductions always contain a certain degree of arbitrariness.

In passing, the recent work of Ellis [6] is to be noted, according to which the visible bands occupy in the infra-red series the place reserved for them in the higher terms. Finally, we should recall the well-known relation of Haber between the ultra-violet and infra-red frequencies.

Some Physico-Chemical Applications.

The Calculation of Heats of Vaporisation.—We agree with Baly that quantum relations are applicable, namely that the energy developed corresponds to a certain number of quanta measured by the frequency of the principal fundamental infra-red band. Table I. shows the kind of agreement which is found.

TABLE I.

	Observed Latent Heat in Calories.	Latent Heat in ergs. per Molecule $\times 10^{13}$.	Principal Infra-red Band.	Frequency of the Infra-red Band. $\times 10^{-13}$.	The Quantum of this Frequency $\times 10^{13}$.	Number of Quanta.	Calculated Molecular Latent Heat.
CS_2	6·384	4·332	4·6μ	6·522	4·278	1	6·305
H_2O	9·650	6·548	6·115	4·906	3·218	2	9·485
CH_3COOH	5·094	3·458	11·50	2·609	1·711	2	5·044
$CH_3CO_2CH_3$	8·166	5·541	7·1	4·225	2·772	2	8·170
$(C_2H_5)_2O$	6·660	4·519	8·75	3·429	2·249	2	6·629
$CHCl_3$	6·984	4·739	8·3	3·614	2·371	2	6·988
CCl_4	7·190	4·879	12·9	2·326	1·526	3	6·744

In a similar way, Ellis [6] has recently sought to ascertain the heat of combination of C—H and N—H, by means of the infra-red spectra of liquids. He has arrived at certain concordant results which are worthy of remark. Thus, for hexane he finds 97,000 calories per molecule for the C—H bond, compared with 92,500 cal./mol. obtained thermochemically. This number, moreover, varies with the type of molecule, reaching the value 117,000 cal./mol. for the bond C—H in benzene. With aniline, the infra-red spectrum gives the value 113,000 cal./mol. for the N—H bond, compared with 101,000 determined thermochemically.

The Energy of Activation of the Molecules.—This energy will be absorbed in the form of quanta of one or more characteristic frequencies in the near infra-red Thus, from the rate of decomposition of a substance in different solvents, and applying thermodynamics, the position of the infra-red bands of this substance in these solvents can be deduced. Amongst others may be mentioned the work on the decomposition in

different solvents of N_2O_5 (Daniels), $(C_2H_5)_3$ S Br (Taylor and Lewis). The agreement between the observed bands and the calculated ones is on the whole reasonably satisfactory.

V. The Principal Problems yet to be Solved.

From what has been said, it is seen that the spectra of liquids are much less connected amongst themselves from a theoretical point of view than are the spectra of gases and solids. Research on liquids is much more complicated than on the other two states of matter : in fact, we meet with intermediate conditions, where considerable intermolecular bonds are to be found. Simple suppositions can no longer be used, for example, the potential energy cannot be expressed as a quadratic function of its co-ordinates, varying linearly with respect to temperature.

The theory of infra-red spectra of liquids thus presents great difficulties ; at the same time, we believe it is possible to say that it would improve considerably if we possessed, relative to the position of the bands, figures sufficiently accurate to enable a choice to be made between different formulæ. What method should be employed in the first place to attain these measurements ? Should one proceed point by point, observing visually the variations of the recording instrument for each wave-length, or would it be better to obtain a continuous curve from a recording instrument ? I have used both methods. The automatic registering instrument is to be recommended for its incontestible qualities of ease, rapidity, and at the same time freedom from personal errors ; we cannot say that the determinations are invariably more accurate than those obtained visually, provided that in the latter the successive points of the readings are near enough to each other.

If, now, one might venture to suggest lines of research one would lay emphasis in the first place on the fundamental question of dispersion. It would be of great advantage, in my view, to have an exhaustive study of the spectra of liquids with a dispersion similar to that used to find fine structure in gases between 1 and 18μ. It would be desirable to determine whether the large absorption bands found with poor dispersion actually possess a large number of maxima and minima similar to those found in gases. It may be added that the technique required to cut special reflection gratings (*échelettes*) appears to have come just in time (Wood, *Phil. Mag.*, April, 1929. See also on this subject Easeley, Fenner, and Spence [24].)

Given that the results from studies of the Raman effect of liquids appear to indicate that the infra-red bands of liquids are made up of a small number of individual lines, a study of the whole subject with a higher dispersion than that used in current work would be very useful ; it would certainly furnish very valuable standards which are at present missing above 3μ in the spectra of liquids.

The second problem to be solved is the measurement of the rotation spectra of liquids. These are still almost unknown, as we have seen, for liquids, and should furnish means of recognising the chemical groups in the molecule, and should also indicate the place which the body occupied in its homologous series. For these purposes it would be advantageous to pursue the study of the spectra of liquids up to the longest wave-lengths possible, of the order 25μ at least. These results appear to be possible with gratings of metallic wires or reflection gratings containing

few lines, because the limit of the practical use of prisms of NaCl and KCl is about 21 to 22μ.

Thirdly, and finally, the measurements on the infra-red spectra of liquids have, up to the present, been largely qualitative, determinations in general being directed more to the ascertainment of the positions of the bands than to their *intensity*. There thus remains a vast field, the exploration which promises to be most fruitful. The principal difficulty is to make cells (with rock-salt sides) sufficiently thin and of accurately-known thickness. On the other hand, it may be observed, in passing, that the thermal receivers (thermopiles, bolometers, etc.), which are generally used in the infra-red, give a direct measurement of the energy (naturally presupposing the best working conditions), whereas, when those regions are studied where photography can be used, the determination of the coefficients of reflection or of absorption requires not only the obtaining of a plate, but its measurement by a microphotometer and a knowledge of the laws governing the darkening of a plate. Thus, the infra-red technique, as it is at present used, greatly simplifies the measurement of the intensity of the bands.

It would be easy to mention numerous problems to which the three above-mentioned subjects of research could advantageously be applied. Among the simplest is the comparison of the spectra in the liquid state with that in the vapour state. Despite the work of Purvis,[23] and Dreisch,[7] it still remains to ascertain what conditions the passage from the liquid state to the vapour state provokes: (1) a displacement of the lines; (2) a variation in their intensity. The first point clearly requires careful measurement because the change, if it exists, is sure to be very small. Reinkober, in very careful measurements, has attacked the analogous problem of the effect of solution on the position of the characteristic frequencies of a solid [25]; another important determination would be to study both qualitatively and quantitatively, the spectra of liquids at various temperatures. With the exception of the measurements of Collins [5] with water, liquids have not been examined, so far as I know, except at room temperature. The formation of an image of the source on the surface of the liquid during an experiment would raise its temperature. In common with others, I have remarked upon the modification of results by temperature which should be taken into account when results are to be co-ordinated. Temperature plays an important part, as we know, in the study of solutions.

At this stage, we may conclude this brief exposition of problems on the infra-red spectra of liquids. The importance of the results already available is seen. At the same time, as has been shown in the preceding pages, a vast field of infra-red regions still remains unexplored, and remains open to theoretical analysis and experimental research.*

* For a more complete bibliography consult *Le Spectre Infra-rouge*, by Jean Lecomte (Paris, 1928, Les Presses Universitaires), or *The Infra-red Analysis of Molecular Structure*, by F. I. G. Rawlins and A. M. Taylor (Cambridge, 1929).

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ON THE INFRA-RED BANDS OF HYDROGEN COMBINED WITH CARBON IN THE MOLECULE OF ORGANIC COMPOUNDS.

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Among the absorption bands in the infra-red spectra of organic liquids that band has been studied with considerable detail whose maximum has been located between 2·9 and 3·8μ. In all the compounds containing the CH_2 and CH_3 groups a band occurs with maximum absorption about 3·4μ, according to the earlier workers, e.g. Julius,[1] Ransohoff,[2] Iklè,[3] Coblentz,[4] Weniger,[5] etc. This band has been attributed, although somewhat vaguely, to the CH_3 and CH_2 groups.

The excellent work of Lecomte [6] follows next in order of time affording in recent years a notable contribution to the qualitative knowledge of the absorption spectra of organic substances in the region of the infra-red.

While the researches of the authors quoted were solely of a qualitative nature, from the point of view of intensity of absorption in relation to the constitution of the molecule, credit is due to Victor Henri [7] as the

[1] Julius, *Verh. Könikl. Akad., Amsterdam*, **1** (1892).

[2] Ransohoff, *Inaug. Dissert.*, Berlin (1896).

[3] Iklè, *Physik. Z.*, 5, 171 (1904).

[4] Coblentz *Invest. of Infr. Spectra*, Carnegie Inst. (1905).

[5] Weniger, *Physical Rev.*, 31, 338 (1910).

[6] Lecomte, *Contribution à l'étude de l'absorption des Rayons Infrarouges*, etc., Paris, 1924. See, *e.g.*, a series of researches in *Comptes rendus* from 1923 to 1929.

[7] Victor Henri, *Etudes de Photochemie*, Gauthier Villars, Paris, 1919.

first to study the bands in a quantitative manner, in an attempt to consider the intensity of the bands at $3{\cdot}4\mu$ as an additive property of the groups CH_2 and CH_3 in the molecule.

A little later the author [8] gave support to the hypothesis that such bands at about $3{\cdot}4\mu$ must be attributed more precisely to the oscillators set up by the CH linkage of the molecule, showing also how in certain simple cases the intensity of the band in question can be expressed as a function of the atom of hydrogen combined with carbon in the molecule. Moreover this interpretation, indicated by the author in 1922 [8] and supported in another paper appearing in 1923, was concurred in a little later by Ellis in 1924 [9] and Dreisch [10] in 1924, and it can be said that all the authors of still more recent work have nowadays accepted this view of the origin of the band at $3{\cdot}4\mu$ in compounds containing hydrogen bound to carbon. Thus recently Pringsheim [11] in a study of Raman spectra discusses the CH band at about $3{\cdot}4\mu$ in the infra-red spectrum. Also the bibliography of more recent papers * reports such an interpretation as if it were not in contradiction with the vague attempts of Julius and Coblentz which did not possess accurate and precise significance.

Experimentally, it is a fact that this band at about $3{\cdot}4\mu$ appears in all compounds containing CH; its intensity in any compound (for instance a hydrocarbon) diminishes as the hydrogen bound to carbon is substituted progressively by atoms of halogens, and totally disappears when all the hydrogen bound to carbon has been so substituted, as has been shown by the author,[12] afterwards confirmed by Smith and Boord [13] for the harmonic of the band of CH at about $1{\cdot}7\mu$.

The recent measurements of the frequencies of maximum absorption in the infra-red spectrum taken from the study of the Raman spectra [11] confirm this in a surprising manner, so far as the infra-red spectra and the position of maximum absorption can be measured in an accurate manner. Such measurements confirmed what the author had already found, namely that the band at approximately $3{\cdot}4\mu$ does not exist in compounds not containing the CH linkage but is always found in those which do possess this bond.

An objection to this interpretation of the $3{\cdot}4\mu$ band has been advanced more recently by F. Bell.[14] In brief, this sole objection to a result on which all the modern authors agree, arises from an erroneous consideration of the significance of the intensity of the absorption, as the second part of the present communication will show, and therefore I do not modify what has up till now been accepted on this interesting question.

Besides the bands of CH in the region of the infra-red spectrum between $2{\cdot}9$ and $3{\cdot}6\mu$, organic liquids show also other characteristic bands such as that at $3{\cdot}0\mu$ (approx.) attributed to the group OH [15] and to the groups NH and NH_2.[16]

* See Jean Lecomte, *Le Spectre Infra rouge*, Paris, 1928.

[8] Bonino, *Atti. Soc. Ligust. Sc. e Lett*, I., IV., Genova, 1922; *Gazz. Chim. Ital.*, 53, 555-582 (1923); *ibid.*, 55, 576 (1925).

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[12] Bonino, *Gazz. Chim. Ital.*, 55, V., 342 (1925).

[13] Smith and Boord, *J. Amer. Chem. Soc.*, 48, 1512 (1926).

[14] Bell, *J. Amer. Chem. Soc.*, 50, 2940 (1928).

[15] Bonino, *Gazz. Chim. Ital.*, 56, 4, 286-300 (1926).

[16] Bonino, *Atti. Soc. Lig. Sc. e. Lett.*, 5, 3 (1926).

In this work it has been the strict intention of the author to recapitulate and co-ordinate the results up to the present time and, with respect to the bands from $2{\cdot}9\mu$ to $3{\cdot}6\mu$, to give a contribution to their study and interpretation.

1. Location of the Band of CH between $3{\cdot}0\mu$ and $3{\cdot}5\mu$ (approximately).

For the precise location of the maximum of the band of CH by the direct method of spectrometric measurement in the infra-red, we have some special sources of error noticed already by all authors who have worked in this field.

Two causes of uncertainty which ought to be kept in mind, are: (*a*) the effect due to the greater or smaller dispersive power of the spectrometer employed. (*b*) The want of coincidence in the dispersion curve of rock salt given by different authors in the region $2{\cdot}5\mu$ to $3{\cdot}5\mu$.

The errors due to cause (*a*) are especially important when we are dealing with resolved bands somewhat close together (as with the double band of alcohol) and to this therefore must be attributed the discordant results that are found in the bibliography. Thus, for the absorption of alcohol between $2{\cdot}9\mu$ and $3{\cdot}5\mu$, some authors, who have worked with a somewhat small dispersion have found a single band, whilst others, Coblentz, Lecomte, etc., using a spectrometer with greater dispersive power, or Ransohoff using a fluorite prism (which has a dispersive power about twice that of rock-salt in this region of the infra-red have distinguished in the same region two absorption maxima, one at $3{\cdot}0\mu$ (approx.) (attributed to OH) and the other at about $3{\cdot}4\mu$ (attributed to CH). This last result agrees also with that recently found by Venkateswaran and Karl [17] from the study of the Raman spectra, also Lecomte [18] in the infra-red absorption spectra of alcohol.

The band of CH between $3{\cdot}2\mu$ and $3{\cdot}5\mu$ changes its exact position in the spectrum according to the constitution of the molecule to which the CH belongs, but nevertheless maintains its wave-length within sufficiently close limits. Thus the position of this band changes as the CH is found in aliphatic compounds or in the benzene nucleus, being at about $3{\cdot}4\mu$ in the saturated aliphatic hydrocarbons and at $3{\cdot}25\mu$ in the benzene nucleus. For the aliphatic CH we can give the following examples :—

Ethane . . .	λ_{IR}	$3{\cdot}39\mu$	Coblentz, *l.c.*, p. 66.[4]
Heptane . . .	λ_{IR}	$3{\cdot}4\mu$	Lecomte, *l.c.*, p. 72.[6]
Higher saturated hydrocarbons . . .		$3{\cdot}43\mu$	Coblentz, *l.c.*, p. 74.[4]

Recently Bonino and Brüll [19] have been able to confirm the position at $3{\cdot}4\mu$ of the band of aliphatic CH in saturated compounds from the examination of the Raman spectra of several hydrocarbons also.

Pentane	λ_{Ra} 3·41
Heptane	λ_{Ra} 3·41
Octane	λ_{Ra} 3·41

On the other hand for benzenoid CH the position of maximum absorption is found at about $3{\cdot}25\mu$: the position found by Coblentz [4] in

[17] Venkateswaran and Karl, *Z. physik. Chem.*, B. 1, Bd. 6, H. 473 (1928).
[18] Lecomte, *Compt. Rend.*, 180, 825 (1925).
[19] Bonino and Brüll. *Gazz. Chim. Ital.*, 9, 59, 1929.

benzene and derivatives and by Lecomte [6] in derivatives of benzene and confirmed by the study of the Raman spectra by Pringsheim and Rosen [11] for benzene and its derivatives, and by Bonino and Brüll [19] for aniline and for mono substituted anilines.

Benzene . . .	$\lambda_{I.R.}$ 3·25μ	(Coblentz, *l.c.*, p. 76.)[4]
Monochloro benzene .	$\lambda_{I.R.}$ 3·25μ	,,
Monobrom ,, . .	$\lambda_{I.R.}$ 3·25μ	,,
Benzene . . .	λ_{Ra} 3·27μ	(Pringsheim and Rosen, *l.c.*)[11]
Monochloro benzene .	λ_{Ra} 3·26μ	,,
Aniline . . .	λ_{Ra} 3·28μ	(Bonino and Brüll.[19])
Dimethyl aniline . .	λ_{Ra} 3·28μ	,,
Monomethyl aniline .	λ_{Ra} 3·28μ	,,

Nevertheless it is interesting to note that the positions of the characteristic bands of CH (aliphatic) undergo a change when the carbon atom is also bound to halogens. This effect is observed very well in the following dicarbon hydrocarbons in which the substitution of a hydrogen by halogen causes a displacement of the CH band towards the smaller wave-lengths.

Saturated liquid hydrocarbons . . .	$\lambda_{I.R.}$ 3·40μ	(Coblentz, *l.c.*).
Ethane . . .	$\lambda_{I.R.}$ 3·39μ	(,,).
Ethylene bromide .	$\lambda_{I.R.}$ 3·35μ	(,, p. 56).
Tetrachlorethane . .	$\lambda_{I.R.}$ 3·35μ	(Bonino, *Z. Physik*, **54**, 11, 1929).[12]
Tetrachlorethane . .	λ_{Ra} 3·35μ	(Pringsheim and Rosen, *l.c.*).[11]

A considerably larger displacement of the CH band is observed when the carbons of such a group contain a double bond. Such variations of the CH band depends on the manner in which the other valencies of the carbon of the CH group are occupied and it can be shown with great precision, especially in the study of the Raman spectra with an ordinary infra-red spectrometer having a relatively small dispersion, that the form of the absorption band and the inferior purity of the spectrum tend to render less certain in this part of the spectrum results which have a displacement less than 0·1μ.

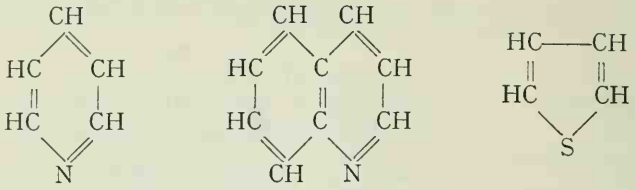
When the carbon has a double bond the CH band is displaced towards the smaller wave-lengths :—

Ethane . . .	$\lambda_{I.R.}$ 3·39μ	(Coblentz, *l.c.*).
Ethylene . . .	$\lambda_{I.R.}$ 3·28μ	,,
Dichlorethylene . .	λ_{Ra} 3·25μ	(Pringsheim, *l.c.*).[11]
Trichlorethylene .	λ_{Ra} 3·25μ	(Bonino and Brüll).
Benzene . . .	$\lambda_{I.R.}$ 3·25μ	(Coblentz, *l.c.*).

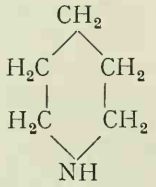
The infra-red band of CH in a group $C{=}\underset{\displaystyle R}{\underset{|}{C}}{-}H$ has, then, the same position as if it belonged more to an aromatic nucleus than to an aliphatic substituted hydrocarbon.

It appears, therefore, that the considerable displacement of the CH band between the paraffin hydrocarbon and benzene does not depend upon the fact that the latter has a cyclic structure, but, apparently, upon the special manner in which two of the four valencies of carbon are bound. This linkage which according to pure chemistry is so dissimilar for ethylene and benzene, from the point of view of pure spectroscopy would seem to be analogous with respect to CH groups.

This conclusion is true also for the CH in heterocylic nuclei. Thus in pyridine, quinoline and thiophene,



which contain the CH in groups such as $C{=}CH$ (with R) we have respectively the maxima of the CH band, according to the measurements of Coblentz,[20] at about $3{\cdot}25\mu$ for pyridine and quinoline and $3{\cdot}32\mu$ for thiophene, while for piperidine



the band goes up again to about $3{\cdot}5\ \mu$, that is to say, to a position like that for CH in saturated aliphatic hydrocarbons.

On the other hand it seems that the hydroxyl group united to carbon together with a CH group does not perceptibly alter the position of maximum absorption of the CH in the range between $3{\cdot}2$ and $3{\cdot}6\mu$. In the presence of the hydroxyl group measurement is somewhat difficult because the hydroxyl shows on its own account a band at $3{\cdot}0\mu$ approximately, which in an apparatus of small dispersion causes the spectrum at $3{\cdot}4$ to be rather vague, thus causing uncertainty in the measurement of the CH band. I choose for this a measurement of Ransohoff which has been made by means of a fluorite prism (having in this part of the infra-red about twice the dispersion of rock salt) which should guarantee greater accuracy.

Propyl alcohol . . .	$\lambda_{I.R.}$ (CH)	$3{\cdot}43\mu$
Ethylene glycol . . .	$\lambda_{I.R.}$ (CH)	$3{\cdot}43\mu$
Glycerine	$\lambda_{I.R.}$ (CH)	$3{\cdot}43\mu$

The CH band, when a valency of the carbon is joined to the hydroxyl group, would therefore seem to be still nearly equal as to its position in the spectrum to that (at about $3{\cdot}4\mu$) of the CH in saturated aliphatic hydrocarbons.

This result seems to be confirmed by the recent research of Venkateswaran and Karl[17] in the Raman spectrum of various aliphatic saturated alcohols for which they find the CH line at $3{\cdot}4\mu$.

Very interesting and curious is the case of compounds containing CH of the two types, that is to say, the type we will call α (like that found in the saturated aliphatic hydrocarbons) and the type we will call β (which from this point of view seems to give a band with a

[20] Coblentz, *loc. cit.*, 96 and 98.

maximum coincident with the CH of the $C=\underset{\underset{R}{|}}{CH}$ group, whether in the aromatic nucleus or in unsaturated aliphatic compounds).

The infra-red spectra obtained for toluene, xylene, picoline, etc., measured with a prism spectrometer, show for the CH group a band the position of the maximum of which is intermediate between the value for CHα and that for CHβ, as can be seen from the following examples :—

Band for CHα . . .	$\lambda = 3{\cdot}43\mu$	
,, CHβ . . .	$\lambda = 3{\cdot}25\mu$	
Toluene	$\lambda_{I.R.}$ $3{\cdot}34\mu$	(Coblentz, *l.c.*, p. 77).
Anisole	$\lambda_{I.R.}$ $3{\cdot}32\mu$	(,, ,, p. 78).

We may therefore ask if this intermediate position depends on the fact that, when the two types of CH are found at the same time in the same molecule, the period of oscillation is effectively altered, or if it is due to the fact that each type of CH gives its own absorption maximum practically unaltered with two distinct maxima, but, on account of the small dispersion of the apparatus, unresolved and apparently fused into one.

This question is not easily solved by the ordinary spectrometric methods of the infra-red, but it seems, from the study of the Raman spectra, that the second hypothesis may be supported, and that in compounds of the type of toluene, etc., containing the two types of CH, we can distinctly show the two frequencies due to each bond.

We come now to an example drawn from the Raman spectrum of toluene studied by Pringsheim and Rosen and confirmed by the author and his collaborator Lazlo Brüll.

Toluene shows in the Raman spectrum, for the CH, not a single line in the infra-red at 3 to $3{\cdot}5\mu$ but two distinct lines which would correspond to a maximum of absorption at $3{\cdot}28\mu$ and another at $3{\cdot}43\mu$. Thus the two types of CH existing at the same time in the same molecule are distinctly shown to have their proper period of oscillation. The author is carefully studying the whole of a series of compounds by means of the Raman spectra to establish whether this conclusion is general.

A final observation on the position of the CH band. If we observe the band of aliphatic CH (type α) in a series of hydrocarbons with increasing number of hydrogen atoms, we observe that, as the number of carbon atoms increases in the molecule so the wave-length of the maximum of the characteristic band of CH between 3 to $3{\cdot}35\mu$ increases equally, finally reaching the limiting value of $3{\cdot}43\mu$ in hexane.

Methane . .	$\lambda_{I.R.}$	$3{\cdot}31\mu$	(Coblentz, *l.c.*).
Ethane . .	,,	$3{\cdot}39\mu$	,,
Butane . .	,,	$3{\cdot}42\mu$	,,
Hexane . .	,,	$3{\cdot}43\mu$	,,

This may be attributed to increasing molecular weight, or state of aggregation, having regard to the manner in which the other valencies of the carbon with which the hydrogen atom is combined are associated in the molecule.

That is to say, the effect of a carbon atom joined by a valency to another carbon atom (or to different atoms) may be to cause a variation in the position of the CH band (cf. the effect on the atom of carbon of the CH bond joined to another atom of carbon by a double bond).

In such questions there is again very little experimental material to establish a criterion accurately. I hope that my most recent researches in progress will soon permit me to make some contribution towards clearing up this point.

With regard to the position of the bands attributed to hydrogen combined indirectly with carbon we may mention the band at 2·95 to 3μ, which is attributed to the OH and NH groups. Some work has been done on this band, but owing to experimental difficulties few definite conclusions can be drawn; brief reference will be made to this matter in the second part of this paper.

2. Intensity of Absorption.

The problem of the quantitative measurement of absorption in infra-red bands presents serious experimental difficulties, but useful information can often be obtained when data are numerous. In the region of the infra-red which we have studied, this difficulty arises chiefly from the entire lack of purity of the spectrum (especially in cases where bands are very close together and each disturbs the measurement of the other), and on the other hand it springs from the manner in which the experimental results are expressed.

Ordinarily these results are expressed by the relation between the intensities of the transmitted and incident rays, but this value does not assist in the study of the relationship between the absorption and the constitution of the molecule. It is more useful and significant to express the data as the molecular coefficient ϵ of maximum absorption given by the formula

$$I = I_0 10^{-\epsilon C d}$$

where I and I_0 are respectively the intensities of the incident and transmitted rays, C the concentration in gram molecules per litre of the liquid under examination, d the thickness in centimetres. This expression of the molecular coefficient of absorption contains implicitly the two laws of Lambert and Beer.

Now the applicability of Beer's law in this field of the infra-red has occupied me for some time.[21] It has been shown that even in the simple case of a solution of benzene in carbon tetrachloride the molecular coefficient of absorption with respect to the CH band does not obey Beer's law, but, rather, a more complex law, which only in the limit of dilute solutions approaches Beer's law.

On the other hand, by studying measurements made in this part of the infra-red in the same liquid at different thicknesses it is found that the absorption coefficient does not remain independent of the thickness as Lambert's law requires. Indeed the variations obtained by us when working with layers of different thickness are larger as the depth approaches the order of magnitude of the wave-length of the infra-red radiation studied. Hence, an extreme delicacy is not possible in the study of infra-red absorption and it is difficult to obtain absolute values. Therefore, measurements which are to be compared with each other should be determined under conditions as nearly similar as possible as regards depth of layer of liquid, purity of spectrum and dispersive power of the apparatus.

[21] *Gazz. Chim. Ital.*, 53, 584 (1923).

From the following measurements under practically identical conditions remarkable regularities are found between the constitution of the substance studied, the value of the maximum coefficient of absorption, and the complex form of the band ascribed to the CH group.[22]

If we attribute a given infra-red band to hydrogen combined with carbon, we must admit that the molecular coefficient of absorption must depend both on the number of CH groups present in the molecule and on the mean probability of any one of the CH groups participating in the absorption: a probability that, other conditions being equal, must depend upon the chemical constitution of the molecule in which the CH is found and upon the characteristics of the medium in which the molecule exists. With this point of view, at the end of 1922, I maintained the necessity of substituting for the theory of simple addition in the infra-red absorption proposed by Victor Henri [7] in 1919, a theory that is at least approximately in line with the above considerations. Thus, while the law of additive absorption requires that a CH group should bring the same contribution to the absorption in whatever molecule it occurred, I maintain that this contribution may differ not only from one kind of molecule to another, but may also vary in the same type of molecule in accordance with the number of CH groups present. Thus it might very well happen (as already shown experimentally by the author in some halogen derivatives of hydrocarbons),[12] that two very similar compounds even containing the same number of carbon atoms in the molecule may nevertheless have notably different absorptions.

The significance of this conclusion (at which the author had arrived at the end of 1923 and 1924 and which was in direct contrast with the idea of simple addition) has not been quite appreciated by Bell [14] in a recent paper in which he attempts to throw doubt on the origin of the band at $3{\cdot}4\mu$ attributed to CH, solely on the ground that two compounds he has studied, which are isomeric and with equal number of CH groups, do not possess the same molecular absorption coefficient, as after all was to be anticipated from the point of view of this paper.

It may be said that the case of dibutyl and di-isobutyl carbonates studied by Bell (which contained the same number of hydrogen atoms, but have different absorptions) is neither the only one nor the first recorded in the literature which show what influence the essential factors have on the contribution that a CH group can make to the absorption and to its probability of participating in this absorption process.

Thus from the measurements of Lecomte we can extract these examples for the band of CH at about $3{\cdot}4\mu$. (The values of ϵ must be regarded as approximate; each of them was obtained by measurements performed with a constant thickness in the layer of absorbing liquid.)

	$\epsilon_{max.}$ for $\lambda = 3{\cdot}4\mu$ (approx.).
Butyl formate	50
Isobutyl formate	39
Propyl phenyl ketone	34·1
Isopropyl phenyl ketone	17·2
Propyl alcohol	35·1
Isopropyl alcohol	31·4

[22] Bonino, *Gazz. Chim. Ital.*, 54, 16 (1924).

to which results we can add those obtained from the paper of Bell :

	$\epsilon_{max.}$ for $\lambda = 3{\cdot}4\mu$ (approx.).
Dibutyl carbonate	56
Di-isobutyl carbonate	31·6

These data confirm the thesis of the writer, namely, that it is not possible to maintain that the infra-red absorption for the CH band at approximately $3{\cdot}5\mu$ is additive, and that while this band must be attributed to the oscillations caused by the atoms of hydrogen combined with carbons, the probability of the various CH groups participating at a given instant in the absorption is strictly dependent on constitutional factors in the molecule. In particular it seems from the examples given that this probability is less with the CH of branched chains than with that of normal chains.

For a series of compounds of a rather simpler nature, the author has endeavoured to find an analytical expression (which would include the criteria indicated above) permitting approximate calculation of the maximum coefficient of absorption for a series of homologous compounds (in the more restricted sense of the word) from the number of CH groups in the molecule. In this research it is supposed (as a first approximation and in conformity with the observations on many absorption bands) that in simple cases in a given series of compounds, the probability that any one CH will participate in the absorption will be inversely proportional to the number of CH groups present in the molecule, and that the constant of proportionality will depend on the particular series to which the compounds in question belongs. We, thence, arrive at a relationship.

$$\epsilon_2 = \epsilon_1 + c \log \frac{n_2}{n_1}$$

where ϵ_2, ϵ_1 are the maximum coefficients of absorption for the CH band at approximately $3{\cdot}4\mu$ of two compounds of the same series having respectively n_2 and n_1 atoms of hydrogen band to carbon, and where c is a constant—not universal or independent of the chemical constitution as erroneously believed by Bell,[14] but closely dependent on this since a given CH at a given instant will participate in the absorption.

Therefore in my two preceeding papers I have explicitly said that even for a series of compounds possessing, from their strictly homologous character, the two features indicated, the constant c must be held to be approximate only " between more or less narrow limits in the series " * and especially " at the lower end of the series," † whence it would be contrary to an exact comprehension of the above formula to consider as equal the constants for two series of compounds, the one with a normal chain and the other with a branched chain, since the constant c is dependent not only on the chemical properties of the compound to which the CH groups responsible for the constant belong, but also on the general constitution of the molecule.

The logarithmic relationship stated above suffices in many cases to represent the maximum absorption coefficient, but it does not provide for the suppression of the absorption coefficient for the CH band when there are no atoms of hydrogen in the molecule bound to carbon. This aspect requires a more extensive relationship of the type

$$\epsilon = c \log (n + 1),$$

* *Gazz. Chim. Ital.*, 55, 336 (1925). † *Ibid.*, 53, 581 (1923).

where c is a constant subject to the same conditions as before, and n is the number of CH groups per molecule; when $n = 0$, then $\epsilon = 0$, hence, absence of absorption. This relationship, within certain limits, thus suffices to represent the maximum absorption coefficient. I give, in Table I., examples of the order of concordance between the calculated and observed values.

TABLE I.

	λmax.	ϵmax. Calc.	Found.
Measurements of Victor Henri.[7] $C = 11{\cdot}40$.			
Ethyl alcohol	$3{\cdot}34\mu$	8·86	7·92
Propyl ,,	$3{\cdot}30\mu$	10·30	10·02
Butyl ,,	$3{\cdot}30\mu$	11·40	11·40
Amyl ,,	$3{\cdot}32\mu$	12·30	12·53
Measurements of Lecomte.[6] $C = 44$.			
Methyl alcohol	$3{\cdot}25\mu$	26·5	25·9
Ethyl ,,	$3{\cdot}40\mu$	35·1	33·3
Propyl ,,	$3{\cdot}40\mu$	39·7	35·1
Butyl ,,	$3{\cdot}40\mu$	44	46
Hexyl ,,	$3{\cdot}40\mu$	50·4	49
Heptyl ,,	$3{\cdot}40\mu$	53	59
Halogenated alcohols (Lecomte's Measurements).[6] * $C = 49$.			
Dibrombutyl alcohol	$3{\cdot}40\mu$	44·3	45·3
Dibromamyl ,,	$3{\cdot}40\mu$	49	47·7
Dibroheptyl ,,	$3{\cdot}40\mu$	54·6	55·6
Measurements of Bonino.[12] $C = 1{\cdot}5$.			
Ethylene bromide	$3{\cdot}35\mu$	1·05	1·02
Tetrachlorethane	$3{\cdot}35\mu$	0·71	0·69
Pentachlorethane	$3{\cdot}35\mu$	0·45	0·49
Measurements of Coblentz (*l.c.*). $C = 9{\cdot}5$.			
Dodecylene	$3{\cdot}53\mu$	13·10	12·50
Pentadecylene	$3{\cdot}53\mu$	14·05	14·10
Hexadecylene	$3{\cdot}53\mu$	14·30	14·67

It is very interesting to note that the hypothesis that the variation of the absorption due to the number of CH groups in the molecule will be inversely proportional to the number of these CH groups proves to be verified; as also does the hypothesis that this variation of the maximum absorption coefficient will be inversely proportional to the square root of the number of CH groups present. This hypothesis can therefore be written

$$\epsilon = c_1\sqrt{n}$$

(where c_1 has the same significance as before), a relation verified sufficiently well in the examples given in Table II. It is possible to give many more examples.

From the results given there is indicated very clearly a great difference in the values of ϵ which we have collated for the same compounds from the measurements of various authors who have worked under different conditions of thickness of liquid layer and purity of spectrum. For the compounds quoted we can state, as a first approximation, that

* The values for I/I_0 were measured graphically from the curve published by Lecomte.

TABLE II.

	λmax.	ϵmax. Calc.	Found.
Alcohols (Lecomte's Measurements). $C = 15$.			
Methyl alcohol	$3{\cdot}25\mu$	25·95	25·9
Ethyl ,,	$3{\cdot}40\mu$	33·5	33·3
Propyl ,,	$3{\cdot}40\mu$	39·6	35·1
Butyl ,,	$3{\cdot}40\mu$	45	46
Hexyl ,,	$3{\cdot}40\mu$	54·2	49
Heptyl ,,	$3{\cdot}40\mu$	58	59
Olefinic Hydrocarbons (Measurements of Coblentz). $C = 2{\cdot}57$.			
Dodecylene	$3{\cdot}53\mu$	12·60	12·50
Pentadecylene	$3{\cdot}53\mu$	14·10	14·10
Hexadecylene	$3\ 53\mu$	14 60	14·67

the absorption for the CH band increases with the number of CH groups present in the molecule and that the variation caused in the absorption by the addition of a CH to the molecule diminishes as the number of absorbing CH groups increases.

From the known measurements we can already deduce that there exists a type of compounds for which, *vice versa*, the absorption for the CH band at $3{\cdot}4\mu$ (approx.) proceeds in a different manner, namely, the variations in the absorption, instead of being inversely proportional to the number of CH groups existing in the molecule or to its square root, are directly proportional, as a first approximation, to the first power. In other words, the contribution added by a single CH group to the absorption will increase with the number of CH groups. Such compounds are the esters for which we have measurements from the recent and important work of Lecomte and from the note of Bell already cited.[14]

For the esters shown in Table III. we find as a first approximation that the maximum absorption coefficient of CH follows a course given by the formula

$$\epsilon = cn^2.$$

TABLE III.

	λmax.	ϵmax. Calc.	Found.
Esters from Lecomte's Measurements. $C = 0{\cdot}25$.			
Ethyl acetate	$3{\cdot}4\mu$	16	15
Propyl ,,	$3{\cdot}4\mu$	25	27·5
		$C = 0{\cdot}20$	
Ethyl propionate	$3{\cdot}4\mu$	20·0	20·6
Propyl ,,	$3{\cdot}4\mu$	28·8	27·6
Carbonic Esters from Bell's[14] Measurements. $C = 0{\cdot}16$.			
Diethyl Carbonate	$3{\cdot}4\mu$	16	15·84
Dipropyl ,,	$3{\cdot}4\mu$	31·4	31·5
Dibutyl ,,	$3{\cdot}4\mu$	52	56

Now, the reason for this difference in behaviour on the part of the esters, first attributed to a special behaviour of the CH in the molecule, must be sought in some more general characteristic as, for example, the complexity of the bands, the possibility of a highly absorbent impurity (traces of water, etc.); only after having removed these causes can we proceed to an interpretation based on the internal mechanism of the CH group as being more or less ready to participate at a given instant in the absorption.

Moreover, consider the quantitative behaviour of the absorption band at 3·0μ belonging to the hydroxyl and NH groups. We can establish that the absorption maxima of this band follow, as regards their intensity, the increase or decrease of the number in the molecule of the respective groups to which the absorption is attributed.

The examples,[16] in Fig. 1, in which is traced the quantitative behaviour of the absorption of the mono-substituted anilines, (C_6H_5 NHR where R is CH_3, C_3H_7, C_4H_9, C_5H_{11}), are worth reporting. These anilines show in the infra-red between 2·9 and 3·4μ two distinct bands: one at 3·0μ (approx.) attributed to NH which is shown in free aniline, and in all the mono-substituted anilines, but not in disubstituted anilines which have no typical hydrogen; another band at 3·4μ attributed to the CH is present in all the anilines. In the substituted anilines, it has not yet been possible to separate this band into the two due to the CH groups of type α and β in the molecule. Now, the band at 3μ remains practically constant in intensity for all the monosubstituted anilines, that is, those containing a single NH while the other band at 3·4μ increases in intensity of maximum of absorption with increase in the number of CH groups, as can be seen from Fig. 1.

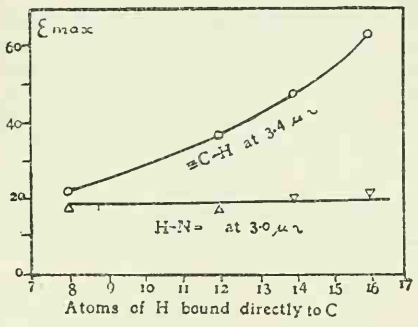


FIG. 1.

From the measurements of Ransohoff [2] for some alcohols and glycols, we can study very distinctly the two bands of OH and CH; we find that in proportion as the atoms of carbon in the molecule, having the hydrogen directly combined with carbon, are replaced by hydroxyl groups, so the intensity of the 3·0μ band attributed to hydroxyl increases, while the CH band at 3·4μ decreases.

	Number of (OH) groups.	λmax.	εmax.	Number of (CH) groups.	λmax.	εmax.
Series with two Carbon Atoms:						
CH_3CH_2OH . . .	1	3·0μ	47·3	5	3·4μ	30·4
CH_2 . OH . CH_2 . OH .	2	3·0μ	54·3	4	3·4μ	28·7
Series with three Carbon Atoms:						
CH_3 . CH_2 . CH_2 . OH .	1	3·0μ	57·4	7	3·4μ	43·2
CH_2OH . CH_2 . CH_2 . OH .	2	3·0μ	68·1	6	3·4μ	40·3
CH_2 . OH . CHOH . CH_2OH	3	3·0μ	70·8	—	—	—

It would be sufficiently accurate from these data to deduce numerical values showing the dependence of the molecular coefficient of absorption on the number of CH and OH groups, because for many of Ransohoff's measurements it has been possible to resolve the two bands of alcohol at 3 and 3·4μ, even although these two bands are sufficiently near ot influence each other. Notwithstanding this, we see also from these a definite result following the variation of the number of active groups in the molecule.

Conclusion.

In this short account of the infra-red bands of hydrogen combined in the organic molecule and especially of the CH group, an attempt has been made to emphasise the significance and chemical interest of the study of this part of the spectrum, and to indicate (as recently shown by Ellis [23] and several years ago suggested by Baladin),[24] the possibility of deducing heats of combination from the position of the various infra-red bands. Also a study of the structure of the bands gives indications as to chemical properties.

From an accurate study of the intensity of absorption, one can obtain an idea as to the probability that a given band may change its proper energy level, thus giving rise to certain chemical consequences.

Moreover, it is useful to extend work on infra-red spectrometry from the chemical standpoint so as to accumulate a large amount of experimental data from which may be studied the structure, as well as the energy and kinetics of molecules.

Many points are still not very certain, others are quite well known; but the study of this field, conducted with vigorous physical methods, and above all, with chemical criticism, should render a great service to chemistry.

[23] Ellis, *Physical Rev.*, **33**, 1, 27 (1929).
[24] Baladin, *Z. Physik*, **26**, 145 (1924).

MOLECULAR ABSORPTION SPECTRA OF LIQUIDS BELOW 3μ.

By Professor Joseph W. Ellis.

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The region of the spectrum below 3μ, although representing a relatively small portion of the total infra-red spectrum, is nevertheless quite significant in the study and interpretation of the absorption spectra of molecules. In particular, the absorption spectra of organic liquid molecules show numerous bands in this region. However, it is not the multiplicity of bands which is of primary importance, but rather the regular recurrence of certain features among the spectra of chemically-related compounds.

At the beginning of an investigation which has extended over a number of years, I observed [1] that absorption bands appeared near $1{\cdot}7$, $1{\cdot}4$ and $1{\cdot}2\mu$ in the spectrum of each organic liquid, as it was plotted in the usual manner from the visual observations of galvanometer deflections. Puccianti [2] had already commented upon the presence of the first of these bands in the spectra of all the compounds which he had studied whose molecules have a hydrogen atom combined with a carbon atom. Guided by this comment, I made the assumption that all three of the above-listed bands were associated with the carbon-hydrogen linkage, inasmuch as this was the only truly molecular feature characteristic of all of the molecules which had been examined. It had been the general, although not the unanimous, conclusion of infra-red investi-

[1] Ellis, *Science*, **54**, 315, 1922.
[2] Puccianti, *Nuovo Cimento*, **11**, 241, 1900.

gators that absorption bands in this region have intra-molecular rather than inter-molecular origins.

Early in the investigation a self-registering photographic method of recording the absorption spectra was substituted for the more laborious method of observing and plotting galvanometer deflections. As a result of this improved method, three other bands were found to recur in these spectra when the proper cell lengths were used. Their wave-length positions were approximately 2·2-2·3, 1·0 and 0·9μ. It was then observed [3] that the frequencies of the six-absorption bands listed in this and the preceding paragraphs, when arranged in the sequence 2·3-2·2, 1·7, 1·4, 1·2, 1·0 and 0·9μ, approximate the following ratios: 3 : 4 : 5 : 6 : 7 : 8.

It was logical to search next for shorter wave-length bands whose frequencies would correspond to 9 and 10 in the above sequence. A few substances for which a sufficient quantity of material could be obtained to yield a 10 cm. layer were examined and the bands sought were readily found [4] near 0·82 and 0·75μ.

The ratios of the frequencies of these eight bands are more accurately expressible by the following: $3(1 - 3x) : 4(1 - 4x) \ldots 10(1 - 10x)$, although the conformity to this sequence of the frequencies of the absorption bands of any one compound is not perfect. When this series is extrapolated [5] to include $2(1 - 2x)$ and $1(1 - x)$, wave-length values of 3·2 and 6·4μ are obtained. In spite of the imperfect agreement, the bands at 3·3-3·4 and 6·7-6·9μ, previously observed by Coblentz [6] in the spectra of a large number of hydrocarbons and hydrocarbon derivatives, were assumed to be these extrapolated members.

Bands in the spectra of some twenty compounds, corresponding to the second, third, . . . and sixth members of the above sequence, were discovered by Márton,[7] who independently arrived at a correlation of these bands identical with the one which I had already presented.

In 1926 Smith and Boord [8] verified the existence of the third, fourth, fifth and sixth members in the spectra of several ethers, esters and related substances. Because this sequence of bands fails to include all of the absorption frequencies characteristic of a hydrocarbon, these authors expressed their doubt as to whether any real significance should be attached to the arrangement.

At about this time doubt as to the correctness of this correlation began to arise in my own mind also. This doubt was not occasioned by the reason advanced by Smith and Boord but for the following five reasons :—

1. The failure of the extrapolated values to check with observed wave-length of the first and second members.

2. The fact that there was not a regular diminution in intensity throughout the sequence ; the bands were approximately paired so far as intensity was concerned.

3. Only the even-numbered members display a regularity in the shifting of bands to slightly different wave-length positions when the spectra of related compounds are compared.

4. Absorption bands in the longer wave portion of the visible spec-

[3] Ellis, *Physical Rev.*, **23**, 48, 1924.
[4] Ellis, *J.O.S.A.* and *R.S.I.*, **8**, 1, 1924.
[5] Ellis, *Physical Rev.*, **27**, 298, 1926.
[6] Coblentz, *Carnegie Inst. Pub.*, No. 35, 1905.
[7] Márton, *Z. physik. Chem.*, **117**, 97, 1925.
[8] Smith and Boord, *J. Amer. Chem. Soc.*, 48, 1512, 1926.

trum, observed a half century ago by Russell and Lapraik,[9] failed to fit in as higher members of the sequence.

5. A study of the absorption of the simplest stable hydrocarbon, methane,[10] in gaseous phase showed clearly that only a part of the bands, corresponding to those observed in more complicated molecules, could be arranged in a single series.

The investigation of the methane spectrum clearly indicated that the band with its centre at $3{\cdot}33\mu$, observed by Cooley [11] and interpreted by him and by Dennison [12] as arising from one of the fundamental modes of vibration of the molecule, was a fundamental band, and not an overtone of a lower frequency band. Bands found at $1{\cdot}69$ and $1{\cdot}15\mu$ were regarded as the first and second overtones of the $3{\cdot}33\mu$ fundamental, while bands at $2{\cdot}32$ and $1{\cdot}37\mu$ were interpreted as combination frequencies arising from another fundamental at $7{\cdot}67\mu$ taken with $3{\cdot}33$ and $1{\cdot}69\mu$ respectively.

With these results in mind the data of the more complicated molecules were re-examined with the purpose of trying a new correlation. It was found [13] that the $3{\cdot}3$-$3{\cdot}4\mu$ band and alternate bands of the older grouping constitute a series with their frequencies expressible,[14] at least approximately, by

$$\nu^n = \omega^0 n - bn^2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ω^0 and b are constants and $n = 1, 2, \ldots 5$. Absorption bands in the visible, recorded by Russell and Lapraik,[9] were observed to fit this new series with values of n equal to 6 and 7.

The molecule for which the greatest number of bands belonging to a single series expressible by equation (1) has been observed is benzene. I have found the eighth member of this sequence as a very weak band in the visible blue region of the spectrum by using a 6·5 meter cell of the liquid and a Hilger El quartz spectrograph. The three other visible bands, in the green, orange and red respectively, which had previously been recorded by Russell and Lapraik, were redetermined and slight errors found to exist in these older values.

Relatively precise data now exist for the wave-length values of the members of this series of benzene bands. The first member has been accurately located at $3{\cdot}27\mu$ by means of the Raman effect by Raman and Krishnan [15] and by others. The second member at $1{\cdot}68\mu$ is probably the least accurately determined of all. Barnes and Fulweiler,[16] using a Thalofide cell and a diffraction grating, have found the third member to be a close doublet with its centre at $1{\cdot}1409\mu$. Using a grating spectrograph, these same investigators have observed the fourth, fifth and sixth bands at 0·8744, 0·7133 and $0{\cdot}6060\mu$ respectively. I have observed the sixth, seventh and eighth members at 0·608, 0·532 and $0{\cdot}476\mu$.

Using the values for these bands as quoted above, with the average of the 0·606 and $0{\cdot}608\mu$ determination for $n = 6$, Table I. has been assembled.

The frequencies ν^n in cm.$^{-1}$ from column 3 of this table have been plotted against their corresponding series member number given in column

[9] Russell and Lapraik, *J. Chem. Soc.*, **39**, 168, 1881.
[10] Ellis, *Proc. Nat. Acad. Sci.*, **13**, 202, 1927.
[11] Cooley, *Astrophys. J.*, **62**, 73, 1925.
[12] Dennison, *Astrophys. J.*, **62**, 84, 1925.
[13] Ellis, *Physical Rev.*, **32**, 906, 1928. [14] *Ibid.*, **33**, 27, 1929.
[15] Raman and Krishnan, *Indian J. Physics*, **2**, 399, 1928.
[16] Barnes and Fulweiler, *Physical Rev.*, **32**, 618, 1928.

TABLE I.

ANHARMONIC SERIES FOR BENZENE.

n.	λ.	ν^n.	ω^n.
1	3·27μ	3,060 cm.$^{-1}$	
2	1·68	5,950	2,900 cm.$^{-1}$
3	1·1409	8,760	2,810
4	0·8744	11,430	2,670
5	0·7133	14,015	2,585
6	0·607	16,470	2,455
7	0·532	18,800	2,330
8	0·476	21,000	2,200

1. The curve obtained is the parabola of Fig. 1. Again, if the differences of the frequencies of the nth and $(n+1)^{th}$ bands, ω^n of column 4, are plotted against the corresponding values of $(n+\frac{1}{2})$ the straight line

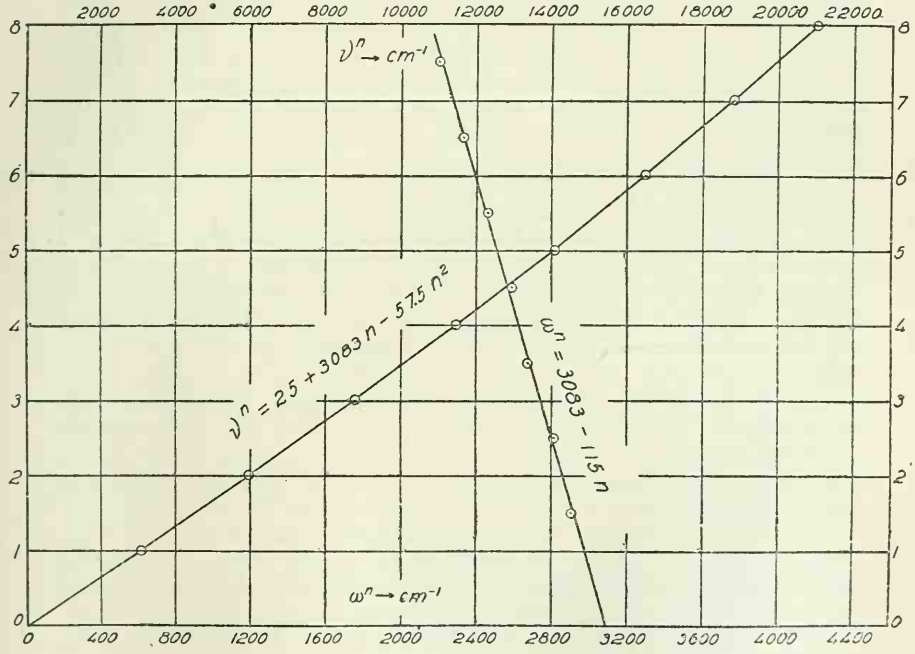

FIG. 1.

of Fig. 1 is obtained. The intercept of this curve on the ω^n axis is $\omega^0 = 3083$ cm.$^{-1}$ and its slope is $2b = 115$. Hence the equation of this line is

$$\omega^n = \omega^0 - 2bn = 3083 - 115n \quad . \quad . \quad . \quad (2)$$

The equation of the parabolic curve, from which the ω^n curve is derived, must then be

$$\nu^n = c + 3083n - 57{\cdot}5n^2 \quad . \quad . \quad . \quad . \quad (3)$$

Evaluation of the constant c from the observed ν^n data of Table I. yields $c = 25$.

Now, under the classical quantum theory equation (2) is the equation of a quantised anharmonic vibrator, ω^n being the vibration rate in spectroscopic units of the oscillator in its nth stationary state; ω^0 then represents the oscillation rate for an infinitesimal amplitude, and n_0 the quantum number of the limiting stationary state at which the oscillator dissociates. The energy of such an oscillator in its nth state is

$$E^n = \omega^0 hn - bhn^2 = 3083hn - 57{\cdot}5hn^2 \quad . \quad . \quad (4)$$

The radiation frequency which is absorbed when the oscillator changes from its zero to its nth stationary state is expressible by

$$\nu^n = 3083n - 57{\cdot}5n^2 \quad . \quad . \quad . \quad . \quad (5)$$

Thus, we see that, exclusive of the small constant term, $c = 25$, equation (3) indicates that the absorption frequencies characteristic of the benzene molecule and included in Table I. probably arise from the molecule, or some part of the molecule, acting as an anharmonic vibrator. The appearance of the constant term is a little surprising, but the data are believed to be accurate enough to establish the certainty of its existence. It has its parallel in the large constant term which appears in the more general band spectra formula and which is caused by a change in the energy of the molecule due to electronic transitions. In this instance, as in the instances where large electronic terms appear, the constant term may arise from a change, probably small here, in the intramolecular configuration.

Assuming that the variable portion of equation (3) arises from a quantised anharmonic oscillator, it is possible to evaluate the dissociation energy of this oscillator by the method devised by Birge and Sponer [17] in the case of nonpolar diatomic gaseous molecules. I have already adapted this method to the case of more complicated molecules.[14] The energy of dissociation D is equal to the maximum vibrational energy which the oscillator can possess. This is given by

$$D = E^n{}_{\max} = h\int_0^{n_0} \omega^n dn = h\int_0^{n_0} (\omega^0 - 2bn)\, dn = h(\omega^0)^2/4b \quad . \quad (6)$$

If ω^n is expressed in spectroscopic units, cm.$^{-1}$, D may be calculated in calories per mole by

$$D = hc(\omega^0)^2 N/4b\mathcal{J} \quad . \quad . \quad . \quad . \quad (7)$$

where N is the Avagadro number, $\mathcal{J}$ the mechanical equivalent of heat in ergs per calorie and c the velocity of light.

For the oscillator giving rise to this particular series of bands in the spectrum of benzene D becomes

$$D = \frac{6{\cdot}55 \times 10^{-27} \times 3 \times 10^{10} \times (3083)^2 \times 6{\cdot}06 \times 10^{23}}{4 \times 57{\cdot}5 \times 4{\cdot}186 \times 10^7}$$

$$= 118{,}000 \text{ cal/mole},$$

or 5·1 equivalent volts.

When the corresponding energies are evaluated for other molecules, for which, however, the optical data are slightly less accurately known, somewhat different values are obtained. Thus for hexane, cyclohexane and chloroform D comes out 97,000, 94,000 and 108,000 calories per

[17] Birge and Sponer, *Physical Rev.*, **28**, 259, 1926.

mole respectively. These variations, however, are very much greater than the experimental uncertainties, and hence represent real differences among these different molecules.

If it is assumed that this series of absorption frequencies from which these energies have been evaluated arises from the carbon-hydrogen bond (*i.e.*, from vibrations of the hydrogen either against the carbon atom or against the remainder of the molecule), the values should check approximately with the heats of linkage of this bond determined thermochemically. The heat of linkage can be determined unambiguously only for the methane molecule. The accuracy of this determination rests upon the accuracy with which the heat of formation of the methane molecule, the heat of dissociation of the hydrogen molecule and the heat of sublimation of carbon are known. Of these, the last-named one has been least accurately determined. Using the following values for these constants respectively, 19,000 [18], 102,000 [19] and 141,000[20], the heat of linkage for a single C-H bond of the CH_4 molecule can be determined from

$$\tfrac{1}{4}(19{,}000 + 2 \times 102{,}000 + 141{,}000) = 91{,}000 \text{ cal/mole},$$

or 3·94 equivalent volts.

Now the regularity in the differences in the heats of combustion among saturated hydrocarbons indicates that the value for the heats of linkage of the C—H bonds is practically the same for all members of the paraffin series. Therefore, there is a justification in comparing the value determined thermochemically for methane with that determined optically for hexane. The 8 per cent. difference between these two values is not surprising. On the contrary, it might be considered surprising that the agreement is as good as it is. For, in the first place, the chemical value represents the average value of the energy necessary to remove each of the atoms, possibly one at a time, from the carbon atom, whereas the optical value probably represents the energy necessary to remove the first hydrogen atom. Furthermore, the optical determination rests upon a moderately long extrapolation of the $\omega^n : n$ curve of Fig. 1 and the assumption is made that the curve remains linear throughout its course. It is known, however, that many curves of this sort which are plotted from the data of diatomic gases deviate considerably, and usually in such a way as to yield too high a value for the heat of dissociation.

It is often difficult to decide what the end products of a dissociation process are. Often one of the constituents is left in an excited state. It is probable, however, that in the present instance the hydrogen comes off as a normal atom inasmuch as the lowest excitation energy of the hydrogen atom is 10·1 volts. The presence of the constant term in equation (3) indicates that the restoring force in the anharmonic vibrator may be slightly different from that of the normal C—H bond. Hence, the dissociation energy which we have evaluated may differ slightly from the true energy of the bond.

It is not surprising to find that the dissociation energies vary somewhat among the different kinds of molecule. This varying energy arises primarily from a variation in the strengths of the bonds of different molecules. The fact that the energies of the C—H bonds of benzene and chloroform are greater than those for hexane and cyclohexane probably

[18] Landolt-Börnstein Tables.
[19] Birge, *Nature*, **121**, 134, 1928.
[20] Kohn and Guckel, *Naturwiss.*, **12**, 139, 1924.

indicates a tightening of these bonds due in the first instance to the unsaturated nature of the phenyl radical and in the second instance to the highly electronegative nature of the substituted chlorine atom.

The absorption bands are in some instances double in those series which are believed to arise from the carbon-hydrogen bonds. In so far as the resolving power of the instruments used has been sufficient to reveal a doubling, it seems that the bands for any one compound are similar throughout the series. Thus, certain of the bands of benzene which have an appreciable width in the spectra secured with instruments of relatively low resolving power appear as close doublets in the records of Barnes and Fulweiler,[16, 21] and of Brackett.[22] In the spectrum of cyclohexane I have observed that the second to the seventh bands are relatively wide doublets with components of approximately equal intensities. The bands of the paraffin molecules are double with unequal intensity components and Brackett's work on the second and third members shows a still greater complexity.

Three explanations of this doubleness have been advanced. Barnes and Fulweiler [21] have assumed that it represents the P and R branches of a single band, thus corresponding to the bands of gaseous molecules. The correctness of this explanation seems doubtful to me. Brackett [22] believes that the two components arise from two types of C—H bond. In the special case of the paraffin molecules he ascribes these components to the primary and secondary C—H linkages respectively. Since I have found a doubling in a more general group of molecules, including cyclohexane, acetone, the methyl group of toluene, xylene, etc., I have been obliged to assume [14] the existence of a difference in C—H bonds more fundamental than that assumed by Brackett. I believe that the absorption bands, at least in many instances, arise from two different types of C—H bond associated with the same carbon atom. This hypothesis finds its best support in the study of Mrs. Lonsdale [23] of the anisotropy of the carbon atom, from which she postulates two each of two types of valence associated with a single carbon atom.

The simplest possible hydrocarbon molecule is the CH molecule. Two electronic bands, at 3900 and 4300 Å.U. respectively, which appear in the emission spectra of burning hydrocarbons are now definitely believed [24] to arise from this molecule. From the structure of these bands the value for the ω° vibration rate has been found to be about 2800 cm.$^{-1}$. This is in sufficient agreement with the 3083, 3000, 2950 and 3110 cm.$^{-1}$ values for benzene, hexane, cyclohexane and chloroform respectively to support the assumption that the absorption bands from which these values of ω° have been obtained really originate in the C—H bonds.

It is probable that most, and it is possible that all, of the fundamental absorption bands of hydrocarbons which are associated with the fundamental vibration rates of the molecule occur in the spectrum with wavelengths greater than 3μ. This means that the bands below 3μ must be interpreted as overtone and combination frequencies.

It is of interest to investigate more closely the bands of benzene in this short wave region. In addition to the harmonics of the $3{\cdot}27\mu$ bands already discussed, there are prominent absorption maxima at 2·7, 2·49,

[21] Barnes and Fulweiler, *J. Amer. Chem. Soc.*, **50**, 1033, 1928.
[22] Brackett, *Proc. Nat. Acad. Sci.*, **14**, 857, 1928.
[23] Lonsdale, *Phil. Mag.*, **6**, 433, 1928.
[24] Mulliken, *Physical Rev.*, **30**, 785, 1927.

2·20, 2·15, 1·4 and 1·0μ. The value of each of these bands compares well with a value obtained from combining the frequency of a member of the 3·27μ series with that of some longer wave-length value selected from the Raman spectrum of benzene as recorded by Pringsheim and Rosen.[25] Thus, the following combinations have been computed and may be compared with observed values included in parenthesis: 3·27 and 16·26μ: 2·72 (2·7μ); 3·27 and 10·48μ: 2·49 (2·49μ); 3·27 and 6·76μ: 2·20 (2·20μ); 3·27 and 6·28 or 6·23μ: 2·15 (2·15μ); 1·68μ combined with this same group of Raman bands would yield combination bands which might be identified with the broad region of absorption around 1·4μ, while combinations arising from 1·14μ and this same group might be associated with the 1·0μ region of absorption.

The question arises whether the spectra of other compounds contain bands which can be associated with definite linked atoms besides the carbon-hydrogen pair. There are such bands in the spectrum of ammonia which also appear with considerable intensity in the spectra of primary organic derivatives of ammonia and with less intensity for the secondary derivatives, but which disappear for the tertiary derivatives. These facts make it fairly certain that the bands originate in the N—H atom pair.

Salant [26] was the first to point out that a band observed by himself and by Bell [27] in the region of 3μ in the absorption spectra of primary and secondary amines was probably to be associated with the N—H pair. He regarded this initially as the first overtone of a band near 6μ, a point of view which he later abandoned as a result of his own further investigation [28] and investigations by myself.[29] The rather extensive studies of the spectra of the amines in the region 1·12μ by Bell,[27, 30] and my observations [29, 31] with much greater dispersion in the region between the visible and 2·5μ have yielded a considerable amount of data in which to study the correlations of bands assignable to N—H bonds.

Such a study has revealed that there probably is a fundamental band near 3μ quite analogous to the 3·3-3·4μ band of the C—H bonds. The first and second overtones occur near 1·5 and 1μ respectively. In one instance,[13] namely aniline, for which a sufficient quantity of the liquid was available to fill long cells, the third and fourth overtones were found at 0·79 and 0·648μ. These four overtones and their fundamental were then shown to obey, at least approximately, the equation of an anharmonic vibrator, equation (1). Furthermore, an approximate evaluation of the energy of the oscillator was made by the method outlined earlier in this paper. A value in fair agreement with that secured thermochemically for a single ammonia N—H bond was obtained.

If these bands which occur in the spectra of the primary and secondary organic derivatives of ammonia are correctly assigned to vibrations within the N—H pair, then these same bands should appear with considerable intensity in the spectrum of ammonia itself. Now the absorption spectrum of ammonia gas has been studied by Schierkolk [32]

[25] Pringsheim and Rosen, *Z. Physik*, **50**, 741, 1928.
[26] Salant, *Proc. Nat. Acad. Sci.*, **12**, 74, 1926.
[27] Bell, *J. Amer. Chem. Soc.*, **47**, 2192, 1925.
[28] Salant, *Nature*, **119**, 926, 1927.
[29] Ellis, *J. Amer. Chem. Soc.*, **49**, 347, 1927.
[30] Bell, *J. Amer. Chem. Soc.*, **47**, 3039, 1925; **48**, 813, 1926; 48, 818, 1926; **49**, 1837, 1927.
[31] Ellis, *J. Amer. Chem. Soc.*, **50**, 685, 1928.
[32] Schierkolk, *Z. Physik*, **29**, 277, 1924.

and by Robertson and Fox [33] throughout the near infra-red including the region below 3μ. In both investigations bands were observed near $1{\cdot}5$ and 1μ. However, in none of the correlations attempted by Robertson and Fox, by Hund [34] and by Hettner [35] have these bands been regarded as overtones of a band near 3μ.

To secure further support for the hypothesis that the $1{\cdot}5$ and 1μ bands are overtones of a fundamental near 3μ I have examined [36] the absorption spectrum of ammonia both in carbon tetrachloride and aqueous solutions in the region below $2{\cdot}5\mu$. It was discovered that with either solvent the $1{\cdot}51\mu$ band retains the position which it occupies in the spectrum of ammonia in gaseous phase as recorded by Robertson and Fox. The $1{\cdot}035\mu$ band occurs at the same place with either solvent, but does not quite agree with the $1{\cdot}023\mu$ band of Robertson and Fox. Because of the broad, weak, irregular nature of the band in the record of

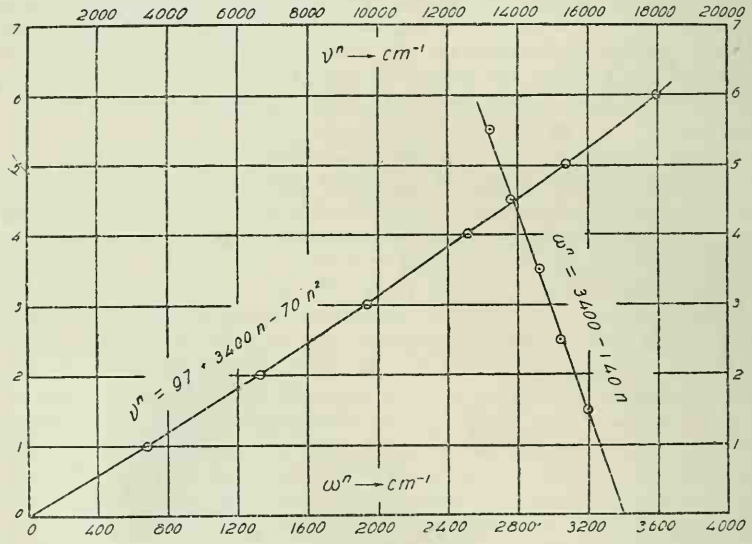

FIG. 2.

the latter investigators, it is not assumed that this slight discrepancy indicates any shift caused by the presence of the solvent.

Because of the agreement between the wave-length values of the ammonia in gaseous phase and in solution it was deemed safe to search for higher overtone bands below 1μ using an aqueous solution. Such bands were found at $0{\cdot}795$, $0{\cdot}652$ and $0{\cdot}556\mu$, the latter two in good agreement with bands found in the very early investigation of Russell and Lapraik.[9]

When the frequencies, ν^n, of the $1{\cdot}51$, $1{\cdot}035$, $0{\cdot}795$, $0{\cdot}652$ and $0{\cdot}556\mu$ bands are plotted against the integer numbers 2, 3, 4, 5 and 6 the parabolic curve of Fig. 2 is obtained. Extrapolation of this curve to include $n = 1$ indicates that the first member of this series should lie near $2{\cdot}9\mu$. Examination of the 3μ absorption region as recorded by Robertson and

[33] Robertson and Fox, *Proc. Roy. Soc.*, A, **120**, 128, 1928.
[34] Hund, *Z. Physik*, **31**, 81, 1925.
[35] Hettner, *Z. Physik*, **31**, 273, 1925.
[36] Ellis, *J. Franklin Inst.* (In press).

Fox and also more recently with still higher dispersion by Stinchcomb and Barker [37] indicates that there are two different bands. The one with a centre at 2·916μ is regarded as the first member of the above series of bands and its frequency has been plotted as $n = 1$ in Fig. 2.

The equation of the parabola of Fig. 2 has been derived in a manner similar to that used with Fig. 1. It turns out to be

$$\nu^n = 97 + 3400n - 70n^2 \quad . \quad . \quad . \quad . \quad (8)$$

As in the former instance a constant term enters the equation. It is much larger than the corresponding term in the equation for the optical frequencies of the benzene C—H series. Again, the tentative explanation of its presence is offered that it represents a slight inter-nuclear rearrangement before vibration takes place in the molecule.

From the constants of the difference curve of Fig. 2,

$$\omega^n = 3400 - 140n, \quad . \quad . \quad . \quad . \quad (9)$$

the dissociation energy of the oscillator has been evaluated by means of equation (7). A value of 118,000 cal/mole, or 5·1 equivalent volts, is obtained. From the best thermochemical data available [36] the average energy associated with a single ammonia N—H bond is 92,000 cal/mole, or 3·99 equivalent volts. The defects inherent in each method of evaluating the energy, mentioned in the preceding discussion of the C—H bond, are present here. In particular is it important to notice that the early optical evaluation of the dissociation energy of the normal N_2 molecule by Birge and Sponer [17] yielded a value 23 per cent. too high. This variation is quite comparable to the 28 per cent. difference between the 118,000 and 92,000 cal/mole values obtained here. In the face of the approximations which have been made in the evaluation of these two energies, it is believed that the agreement is sufficiently good to identify the N—H pair as the anharmonic oscillator giving rise to the 2·916, . . . 0·556μ series.

Wood [38] has just studied the Raman spectrum of ammonia gas at atmospheric pressure. He found a single type of modified line associated with 4046, 3663, 3654, and 3650 Å.U. as exciting lines. The frequency of the separation between the incident and the scattered line was in each case about 3330 cm.$^{-1}$. It is interesting to note that this is the value obtained from equation (8) by dropping the constant term and letting $n = 1$. In other words, the only infra-red frequency which appears in the Raman spectrum of ammonia is one near 3μ. But this differs from that assignable from observations to the fundamental vibration of the N—H group, by an amount equal to the constant term of the formula used to correlate this fundamental with its overtones.

All of the bands in the near infra-red and visible absorption spectrum of ammonia can be rationally correlated [36] on the basis of three fundamental frequencies. In addition to the one with its center at 2·916μ considered above, the strong bands at 10·55 and 6·132μ are chosen as fundamentals. The 6·13μ band is of interest inasmuch as there is much evidence pointing toward the existence of a corresponding band in the spectra of the amines. Again, bands appearing near 2·0 and 1·2μ in these latter spectra are interpreted analogously to corresponding bands in ammonia, namely, as direct additive combinations of the 6μ fundamental with the 3μ fundamental and its first overtone at 1·5μ respectively.

[37] Stinchcomb and Barker, *Physical Rev.*, **33**, 305, 1929.
[38] Wood, *Phil. Mag.*, **7**, 744, 1929.

The discussion of the preceding paragraph indicates considerable similarity between the spectra of molecules containing C—H and those containing N—H bonds. For associated with each type of bond there seem to be two fundamental bands, near 3·3-3·4 and 6·7-6·9μ for C—H and near 3 and 6μ for N—H, the shorter wave fundamental in each instance having an anharmonic series of overtones and the latter having few, if any, overtones. In each instance the longer wave fundamental enters into direct combination with the shorter wave fundamental and its overtones.

There are still other linked pairs of atoms in certain molecules with which there can be correlated certain near infra-red absorption bands. Investigations by Bell [39] and by myself [40] have shown that absorption maxima which appear at 3·9 and 2·0μ in the spectra of mercaptans but which are not present in the spectra of corresponding sulphides are probably fundamental and first overtone bands associated with the S—H bond.

The studies of Bonino [41] and of Sappenfield [42] indicate that corresponding bands at 3·0 and 1·55μ in the spectra of alcohols are assignable to the O—H linkages. Whether these have any intimate relation to similar bands in water is an open question.

I have shown [43] that there is much evidence for believing that the C=O linkage in the aldehydes, ketones and esters is responsible for absorption bands in the spectra of these compounds near 5·9, 2·9, 1·9μ, etc.

The early assumption [44] that there is a linear series of bands characteristic of the C—C linkage beginning at 28μ is probably incorrect. Also, although it is quite certain that there are absorption features resulting from the presence of carbon-halogen bonds in a molecule, it is doubtful whether my former correlation [45] of such bands is the correct one.

In conclusion, although the results summarised in this paper seem to indicate clearly that many of the outstanding features of near infra-red absorption spectra are associated with localised portions of the molecule, nevertheless complete interpretation of detailed bands which occur must await further analysis with instruments of greater precision than have been generally employed. The investigations of Brackett [22] primarily and of Easley, Fenner and Spence [46] have shown the desirability of using spectroscopes of high resolving power in work of this sort. It is my intention to continue the study of the infra-red absorption spectra of organic liquids with a spectrograph of higher resolving power than I have used heretofore.

[39] Bell, *Ber.*, **60**, 1749, 1927 ; **61**, 1918, 1928.
[40] Ellis, *J. Amer. Chem. Soc.*, **50**, 2113, 1928.
[41] Bonino, *Gass. chim. ital.*, **53**, 575, 1923.
[42] Sappenfield, *Physical Rev.*, **33**, 37, 1929.
[43] Ellis, *J. Amer. Chem. Soc.*, **51**, 1384, 1929.
[44] Ellis, *Physical Rev.*, **27**, 298, 1926. [45] *Ibid.*, **28**, 25, 1926
[46] Easley, Fenner and Spence, *Astrophys. J.*, **67**, 185, 1928.

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PART III. (B).—INFRA-RED SPECTRA OF GASES.

INTRODUCTORY PAPER.

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This introduction purports to afford the student a brief summary of the history and development of work in the infra-red, chiefly as applied to the investigation of gases, with special reference to work insofar as it has a bearing on chemical problems.

Historical and Apparatus.

That radiations existed beyond the red end of the visible solar spectrum was shown by the elder Herschell in 1800, when he placed a thermometer in that region and obtained maxima and minima of temperature in his instrument, while forty years later his son deduced the existence of emission bands in the same region from discontinuities observed in evaporation from a blackened surface wetted with alcohol. Another forty years elapsed before Langley made explorations by an instrument of precision, the bolometer, to be shortly followed by other delicate indicators, such as the radiometer of Crookes, the radiomicrometer of Boys, and the thermopile used in conjunction with a galvanometer for receiving and measuring the small quantities of energy passing from a dispersing prism or grating. By such instruments the sun's spectrum was explored, and when methods were evolved for establishing wave-lengths, it soon came to be realised that the position of bands in the infra-red had some relation to constituents of the molecule. To give examples, Abney and Festing,[1] by photography in the region just beyond the red end of the spectrum, had been impressed by the relation between their bands and the occurrence of certain organic radicles (in liquids), and Ångstrom [2] and Julius,[3] both using a bolometer, investigated organic liquids and tried to identify the wave-length of the bands present. Aschkinass [4] and Paschen [5] investigated water-vapour, and Ransohoff [6] the effect of the OH radicle. Rubens and Aschkinass [7] worked for the first time up to 20μ with a sylvine prism on CO_2 and H_2O vapour. Benzene derivatives were investigated by Puccianti,[8] who deduced from his results that absorption depends on the groups of atoms which exist in the molecule. Thus, before Coblentz [9] published the first large instalments of his results on absorption, emission, and reflexion in the infra-red in 1905, 1906, and 1908, workers had appreciated the point of view

[1] *Phil. Trans.*, **172**, 887 (1882).
[2] *Ofersigt Af Kongl. Vetenskaps-Akadem. Förhandl.*, Stockholm, S. 549, 1889; S. 549, 1889; S. 331, 1890.
[3] *Verhandl. Konikl. Akad.*, Amsterdam, Deel I., No. I., 1892.
[4] *Ann. Physik* (3), **55**, 406, 1895. [5] *Ibid.*, **53**, 336, 1894.
[6] *Inaug. Diss.*, Berlin, 1896.
[7] *Astrophys. Jour.*, **8**, 181, 1898.
[8] *Nuovo Cimento*, **11**, 241, 1900.
[9] *Publ. of Carnegie Institute*, Washington.

that elucidation of molecular structure might come from investigations of spectra in the infra-red.

Coblentz, from his work, mostly on liquids, although also on gaseous hydrocarbons, ethers, ammonia, and oxides of carbon and sulphur, confirmed this point of view and associated with various groups, such as CH_2, NH_2, NO_2, OH and NCS, certain bands which he found in the infra-red spectrum up to about 15μ.

The region of the near infra-red is usually taken as that lying from the end of the visible spectrum, at about 7500 Å., or $0{\cdot}75\mu$, which is equivalent to a wave-length of 0·00075 mm. as far as 23μ, this being the limit of usefulness of dispersing prisms. Beyond this, in the far infra-red coarse gratings have been used, but for the most part reflexion from polished plates of crystals, the method of *Reststrahlen*, up to 200 or 300μ, developed by the school of Paschen and Rubens.

Most of the work has been done in the near infra-red, and for its accuracy spectroscopists in this region are indebted to Paschen and his collaborators for their accurate determination of the refractive index of quartz, fluorite, rock-salt and sylvine, for which, in the order named, their dispersion is most favourable in the regions 0·8 to 3μ, 3 to 8μ, 8 to 16μ, and 16 to 23μ. With early prism apparatus it was found that when wave-length was plotted against absorption, definite bands or peaks were found in certain regions; later, by using the appropriate prisms, these bands became resolved into a series of peaks, until to achieve the best resolution, gratings in conjunction with a prism were employed to bring out fine structure in a band.

For accuracy in this type of work, very considerable attention has to be paid to technique, but here no more than mention can be made of certain precautions. Such are, the necessity for ensuring a constant source of radiation, the maintenance of parallelism in the windows of the containers for the absorbing media, the need for taking strict account of the temperature of the prism since its refractive index changes with temperature, the calibration of the markings on the prism table or wave-length drum, securing a highly sensitive thermopile and galvanometer, and the frequent calibration of the assembled instrument against standard lines, or if a grating, by the order of the spectrum.

A description of the instruments used will be found in Baly's "Spectroscopy," Vol. I. (1924), and details as to technique with a prism instrument and precautions to be observed in Parts I. and II. of "Studies in the Infra-red Region of the Spectrum," by Robertson, Fox, and Hiscocks.[10] Recent descriptions of methods of using a grating are given in "Infra-red Investigations of Molecular Structure, Part I.," by Snow and Taylor,[11] and in "The Infra-red Spectra of Gases under High Dispersion," by Barker and Meyer, communicated to this General Discussion.[12]

For a short distance beyond the visible red, photography has been used, but even with specially sensitised plates the limit is little beyond 1μ. In Baly's "Spectroscopy," Vol. II. (1927) will be found an account of methods of sensitising plates for use beyond the visible spectrum. By making use of the evaporation of naphthalene on a celluloid film, Czerny[13] has quite recently succeeded in obtaining bands up to 6μ. As the phosphorescence induced in certain preparations of zinc sulphide containing definite impurities, is quenched by infra-red radiation, this

[10] *P.R.S.*, **120**, 128, 149 (1928).
[11] *P.R.S.*, **124**, 442.
[12] P. 912.
[13] *Z.Physik*, **53**, 1 (1929).

method has also been tried for the detection of emission and absorption bands, but the results, while interesting, are somewhat lacking in definition, at least, as regards absorption.

Meaning of Infra-red Bands.

Approaching the question from the theoretical side, Drude,[14] in 1904, from the conception of vibrating charged particles, by working on the dispersion formula of various crystals obtained the result that if any position be chosen for a wave-length in the ultra-violet there must be a corresponding wave-length in the infra-red. The small particles demanded for producing the effect in the ultra-violet (recognised as the electron after its discovery by J. J. Thomson) fixed the size of the particles affecting the infra-red. This size corresponds with that of atoms and molecules. All recent work confirms that the band spectra found in the infra-red region arise from atoms and molecules; or, more strictly, in this region they reflect transitions in the oscillations of the atoms of a molecule and transitions in the rotation of the molecule itself. Electronic transitions are for the most part detected by effects in the visible or the ultra-violet portions of the spectrum, but as contributions of all three types of energy, electronic, oscillatory and rotational, inter-react, there may be found in the infra-red spectrum evidence of electronic changes.

Oscillation Bands.

The earliest bands found in the infra-red appeared as maxima of emission or absorption, and as the apparatus then was not high in resolving power, when plotted, they took the form of smooth peaks the maximum of which was usually fairly well defined. When the maximum is calculated from the mean of the band, it is of course advisable to plot on a frequency or wave-number basis. It was early found, for example, by Coblentz, that in many cases these bands are harmonics of a fundamental frequency. The explanation of these harmonic absorption bands is somewhat as follows: radiation falls on the molecules whose nuclei are supposed to be vibrating to and from each other; when the radiation falls on the molecule it is absorbed, in quanta ($h\nu$) as it appears, according to the characteristic frequency of the vibrating components, and further, as the nuclei are not removed sufficiently far from one another to obey a pure sine law defining their period, this departure from a pure sine law permits of a Fourier analysis and so the vibration is resolved into a fundamental and harmonics representing one, two, three quanta, etc. We shall see presently that this has to be slightly modified when rotation of the molecule is also taken into consideration.

Rotation Bands.

These may either be considered separately, or chronologically, as they have been found imposed on oscillation to form oscillation-rotation bands. Leaving for the moment the chronological development, we may start with Somerfeld, who considered the case of a diatomic molecule of moment of inertia $\mathcal{I}$, rotating round an axis perpendicular to the line joining the atoms, with an angular velocity ω. Applying the principle of Bohr, he quantised the moment of momentum, so that each quantum jump represents a change in the moment of momentum. If the moment

[14] *Ann. Physik*, **14**, (4), 677 (1904).

of momentum then is taken as a whole multiple of $\frac{h}{2\pi}$, $\mathcal{J}\omega = \frac{mh}{2\pi}$, and $E_{\text{kin}} = \frac{h^2}{8\pi^2\mathcal{J}} m^2$; by the Bohr-Einstein conception

$$h\nu = E - E_1 = \frac{h^2}{8\pi^2\mathcal{J}}(m^2 - m_1^2),$$

and by the principle of selection m can change by ± 1 or 0. Then

$$\nu = \frac{h}{8\pi^2\mathcal{J}}(\pm 2m + 1),$$

whence the spacing difference is $\frac{h}{4\pi^2\mathcal{J}}$, a result in accordance with facts. It will be seen that by putting the spacing difference $\Delta\nu = \frac{h}{4\pi^2\mathcal{J}}$, the moment of inertia of the molecule can be calculated and, from the moment of inertia, the masses of the vibrating atoms being known, the length of the molecule. The length of the molecule thus calculated has been compared in several cases, notably for diatomic molecules, with values obtained in other ways, such as from the kinetic theory of gases or from their viscosity, a fair agreement being obtained. More recently, half-quantum numbers have been introduced $(m - \frac{1}{2})$ being written for m and this leads to $\nu = \frac{h}{8\pi^2\mathcal{J}}(2m)$, that is without the constant term. In some cases no constant term is found (*cf.* Czerny for HCl rotation bands about 60μ) [15] pointing to the existence of half-quanta.

Pure rotation bands are found towards the end of the near and in the far infra-red. Thus, they have been found for water vapour (*cf.* Hettner) and for HCl (*vide supra*), the spacing in the region of 60μ in the case of HCl being nearly the same as that imposed on the oscillation band at 3·46μ.

Oscillation-rotation Bands.

In the region of the near infra-red, and especially towards the visible region of the spectrum, more refined instruments show that the bands possess a fine structure. The chronological development of the theory of such bands is of interest. Rayleigh,[16] assuming on the basis of classical mechanics a Maxwellian distribution of velocities, in 1892 showed that an oscillator emitting and absorbing at a frequency ν_o due to its oscillations alone, would when rotating about an axis perpendicular to its line of vibration with a frequency ν_r, emit or absorb at the new frequencies $\nu_o + \nu_r$ and $\nu_o - \nu_r$. This seemed at first to meet the case, as in some of the early bands such as those of Burmeister two broad areas appear which the Maxwellian distribution of rotational velocities would require. In 1911, however, Nernst concluded that the rotation must also be quantised, and in 1912 Bjerrum, and E. v. Bahr, 1913, resolved a band of HCl into a series of small bands, which they ascribed to the effects of rotation of the molecule. This band has been better resolved by Imes and others, and from the spacing of the fringes the diameter of the molecule of HCl has been calculated and found to agree with values obtained by quite distinct methods. The calculations of the last section

[15] *Z. physik. Chem.*, **34**, 227 (1925). [16] *Phil. Mag.*, **24** (5), 410 (1892).

can now be applied so far as rotation is concerned, to the fine structure found on these oscillation bands and a comparison can be made as between the moment of inertia so deduced and that derived from energy relations, as for example by Imes [17] for HF, HCl and HBr, and for NH_3, PH_3 and AsH_3 which, however, give higher results.

As both oscillation and rotation are quantised in an oscillation-rotation band, the quantum condition is

$$h\nu = \nu_o(n - n')h + \frac{h^2}{8\pi^2\mathfrak{J}}(\pm 2m + 1),$$

on the assumption that the moment of inertia remains unaltered. Such a formula would indicate a fundamental with exact harmonics, each band having three branches, those towards the shorter and the longer wave-lengths with rotation fringes $\frac{h}{4\pi^2\mathfrak{J}}$ apart (R and P branches), and a third, the Q branch, which may either be absent (if $m = 0$) or removed from the centre by a quantity equal to the constant term $\left(\frac{h}{8\pi^2\mathfrak{J}}\right)$.

But, apart from the above formula being applicable only when there is one moment of inertia, it is not found that the centres of the bands are in exact harmonic ratio. Kratzer [18] treats this in the following manner.

By reason of the fact that the oscillations are such that the nuclei are not removed sufficiently far to be outside their mutual influences, the law of force which they obey will not be that of inverse squares. So a vibration of two atoms in a dipole, for example, will not have a sine law defining its period. This departure from a true sine law permits by a Fourier analysis, of the resolution of the vibration into a fundamental and harmonics. These might be true harmonics, but Kratzer sets out to show that they are out of tune by a small quantity. He does this by assuming a general law of force on the basis of inverse powers of the distance between the two nuclei. This he integrates to get the energy involved, and then links it up with the rotation according to the Hamilton-Jacoby differential equation. Having then got a general expression for the energy involving transverse vibration and rotation, he applies the conditions for each degree of freedom. This leads to an expression which can only approximately be integrated, but which, on simplification, comes down to $\frac{W_o^n}{h} = n\nu_o(1 - nx)$, that is, if ν_o is the fundamental, the harmonics are derived from it by whole numbers with a small correction for each harmonic.

Essentially, this deviation from true harmonics, is due to the compounding of rotation and transverse vibration.

Electronic Bands.

Although electronic transitions give rise to effects which are usually manifested in the ultra-violet or the visible regions of the spectrum, special conditions in the molecule may lead to their detection in the infra-red. Such a condition obtains in the gas NO which is chemically interesting from reactivity due to its unsaturatedness and from the point of view of structure, as it has an odd electron. When the funda-

[17] *Astrophys. Jour.*, **50**, 251 (1919). [18] *Z. Physik*, **3** (3), 289 (1920).

mental of NO in the infra-red is resolved as it has been by Snow, Rawlins, and Rideal,[19] a central (or Q) branch is found which they attribute to the electronic angular momentum about the axis of figure. A comparison of the spectroscopic features of such molecules with those which, like HF, HCl, HBr and CO, have their electronic orbital angular momentum parallel to the axis of figure is made by C. P. Snow (p. 930 of this Discussion).

Emission Spectra of Gases.

Much less work has been done on the emission spectra of gases than on their absorption. Paschen [20] and Rubens and Aschkinass [21] investigated the emission bands of CO_2 and H_2O, which have an importance in connexion with combustion (*cf.* the work of Garner and his school). Strong emission bands were found by Runge and Paschen in helium.[22] Coblentz [23] examined the emission spectra of H_2, O_2, N_2, CO, CO_2, H_2O, NH_3 and C_2H_5OH, finding strong bands for N_2 from the end of the visible up to $1{\cdot}06\mu$. Water was found to have no emission bands, although bands were found with C_2H_5OH.

For the purpose of calibration of infra-red spectrometers, the emission bands of mercury determined by Paschen, especially the well-defined band at $1{\cdot}014\mu$,[24] have proved of great service, and others might be found equally useful.

Information given by Infra-Red Spectra of Gases.

Under the following headings are noted examples of such information as is given by a study of infra-red spectra, especially with regard to the constitution of the molecules and their chemical aspects.

(1) *Absence of Bands in the Infra-red.*

In the case of simple gases such as hydrogen, oxygen, chlorine, bromine and nitrogen, the presence of bands in the infra-red has not been confirmed. As the atoms constituting these molecules are similarly placed, it is assumed that there is no electric moment between them nor deformation, and consequently no absorption is found in the infra-red.

(2) *Frequency of Oscillation.*

Knowledge of the frequency of oscillation is important, as it affords a guide in the attribution to certain frequencies of the most probable oscillation of atoms in a molecule when there are several degrees of freedom available. That such a choice may be in the direction of correlating the movements of heavier portions of the molecule with slower frequencies is supported by the following direct information from two sets of similar molecules, each of ascending molecular weight, the one set having only one, and the other more than one fundamental frequency.

Thus, in molecules of similar constitution in which one atom increases progressively in mass, it is found that the fundamental infra-red oscilla-

[19] *P.R.S.*, **124**, 453 (1929).
[20] *Ann. Physik* (3), **53**, 324 (1894).
[21] *Ibid.*, **64**, 584 (1898).
[22] *Astrophys. J.*, **3**, 4 (1896).
[23] Carnegie Institution, 308 (1905).
[24] Paschen, *Ann. Physik* (4), **27** (1908); Paschen, *Ann. Physik*, **36**, 197 (1911); Dingle, *Proc. Roy. Soc.*, **100**, 167.

tion band of the series decreases in frequency with increasing mass of that atom. Examples are found in the case of HF, HCl, HBr and HI,[25] which respectively have for ν_0, 4003, 2939, 2590 and 2272 cm.$^{-1}$, and of NH_3, PH_3 and AsH_3,[26] which have for one of the fundamentals the wave-numbers (cm.$^{-1}$) respectively 1630·9, 1125·0 and 1005·4.

The presence of simple multiples of frequency (harmonics) and the resolution of frequencies into combinations of the frequencies of two or more fundamentals, often come for consideration into questions of molecular structure.

(3) *Frequency of Rotation.*

From the frequency of rotation can be calculated, at least for the simpler molecules, the moment of inertia, and from this the length of the molecule, or approximately the distance of one atom from the others. Values thus obtained may be compared with those derived in other ways, as from the kinetic theory of gases[17] or from viscosity,[27] and many instances of good concordance have been found.

It is of interest to note that the moment of inertia obtained from observations of spacing of fine structure in the infra-red [28] has been found to agree with the same constant, for example in NO from work by ordinary spectroscopic methods.

As with oscillation so the frequency of rotation in a similar series slows down with increasing mass of the characteristic atom, as is shown in the case of HF, HCl, HBr and HI which have a frequency of rotation corresponding to $\Delta\nu = 41{\cdot}1$, 20·8, 16·7 and 12·8 respectively (*l.c.*) and in the case of NH_3, PH_3, AsH_3 the corresponding values of 19·9, 11·5 and 10·0 or 8·5 wave-numbers (cm.$^{-1}$) respectively (*l.c.*).

As examples of the distance apart of the atoms in the above hydrogen halides may be quoted the following values calculated from the spacing distances of the rotation bands by way of the respective moments of inertia: for HF, $0{\cdot}923 \times 10^{-8}$, for HCl, $1{\cdot}282 \times 10^{-8}$, for HBr, $1{\cdot}42 \times 10^{-8}$ and for HI, $1{\cdot}616 \times 10^{-8}$ (*l.c.*).

(4) An *Electronic Rotation* which has been referred to above occurs only in special cases when there is an unbalanced electronic system.[28] The result is to produce a Q branch due to the gyroscopic character of the motion round the axis of figure.

(5) *Relationship with Physical Constants.*

Moment of Inertia, derived from rotation transitions, and length of molecule derived therefrom have been described above.

Atomic and Molecular Heat.—The first correlations between atomic or molecular heat and a characteristic vibration frequency lying in the infra-red were made by Einstein, Nernst, Lindemann, Haber, and later by Debye, but these were for solids. Bjerrum, in 1914, from the known infra-red bands of CO_2 and H_2O, deduced the value of C_v with fair agreement, and Eva v. Bahr showed the dependence of the breadth of the band on temperature.

More recently a relation between the moment of inertia of a molecule and the specific heat of a gas has been formulated by Eucken, Karwat,

[25] Czerny, *Z. Physik*, 44, 235 (1927).
[26] Robertson and Fox, *Proc. Roy. Soc.*, **120**, 189 (1928).
[27] *Ibid.*
[28] Snow, Rawlins, and Rideal, *P.R.S.*, **124**, 453 (1929).

and Fried,[29] and this matter has been discussed by Rawlins.[30] From the oscillation and rotational frequencies of two bands of HCl, Hicks and Mitchell [31] have calculated the specific heat and entropy of the gas.

(5*a*) *Relation to Optical Dispersion.*

It is well known that for complete specification of the optical dispersion of a gas the general formula

$$(n^2 - 1) = \sum \frac{A\lambda^2}{\lambda^2 - \lambda_1^2}$$

may be applied. Where the gas has no bands in the visible or near infra-red it is sufficient to chose two constants, A and λ_1, or to take two terms of the summation, one of which will take account of the dispersion electrons and the other of the natural frequency of the molecule or its atoms. A one-term formula will fit the observations of refractivity for air, since there are no bands as far as 13μ. If, however, we are dealing with a gas like CO_2 with several bands up to 15μ, it is necessary to use one term at least to take account of each band. A formula containing five terms was used by T. Wetterblad [32] to express the dispersion of CO_2 down to 14μ, and it fits the observations with fair exactness. The curve obtained from plotting Wetterblad's observed refractivities shows in a striking manner the region of anomalous dispersion in the neighbourhood of band $4{\cdot}27\mu$ of CO_2. There are few reliable observations of refractivity in the infra-red region; nevertheless, dispersion curves should fit the observations best when the near infra-red bands are considered in the dispersion formula.

It is further to be noted that when Wetterblad's five-term dispersion formula is extrapolated to $\lambda\infty$, the results agree much better with the known value for the dielectric constant than comparison with the dispersion for the visible spectrum alone.

This agreement in some cases between the results deduced from dispersion formula involving infra-red bands, and the dielectric constant must not be pushed too far; for with many gases such a O_2, N_2 no near infra-red bands are known and a dispersion formula cannot therefore be constructed to take in infra-red bands. The dielectric constant may, however, be utilised to calculate moments of inertia for diatomic substances provided the distance between the nuclei can be ascertained in some other way.[33] This furnished a check on $\mathcal{J}$ as calculated from infra-red bands. Another check on this constant is obtained from the specific heat variations with temperature.[34]

(6) *Energy of Dissociation.*

Important results on the energy of dissociation of molecules from the frequency of infra-red vibration bands are to be obtained from the examination of the fine structure of bands in the visible and ultra-violet spectra. The most general formula of band spectra of molecules contains differences of terms representing vibration. One of these terms of the formula refers to the normal molecule, and has been represented by

[29] *Z. Physik*, **29**, 1 (1924). [30] *Proc. Physical Soc.*, **38**, 176 (1926).
[31] *Jour. Amer. Chem. Soc.*, 48, 1520 (1926).
[32] T. Wetterblad, *Dispersionsmessungen im Ultrarot*, Upsala, 1924.
[33] Joachim and Wisnienski, *Z. Physik*, 1927, **47**, 392.
[34] Dennison, *P.R.S.*, 1927, **A. 115**, 483.

V. Henri [35] by the expression for oscillation, $T_0(p_0) = p_0\alpha(1 - p_0x)$, which converges to a maximum when α is in wave-numbers cm.$^{-1}$. In such a case (following Franck), the energy of dissociation of the normal molecule into normal atoms is given by $D_0 = T_0(p_0)_{\max}hc$. By utilising other vibration terms, the energy for dissociation of the normal molecule into normal and active atoms may be calculated.

This subject has formed the object of an extensive and important inquiry by R. T. Birge,[36] who applied the limiting value of the energy of vibration, namely

$$E_n = D = h\int_0^{n_0}\omega_n dn$$

to calculate D for O_2, O_2^+, N_2, N_2^+, CO, CO^+ and NO. A new method of deriving accurate heats of dissociation from band spectra has now been worked out by Birge, depending upon the plotting of the frequencies of vibration in a particular manner which is described in his communication to this Discussion.

(7) *Identification of Oscillation Bands with Chemical Linkages.*

For the chemist it is of the greatest interest to know if any of the degrees of freedom of the atoms in a molecule can be identified with the bonds which he is accustomed to consider as linkages within the molecule.

Since the days of the earlier investigators who regarded the chemical radicles or groups as resonators, the point of view has changed under the influence of the quantum theory, in the direction of considering definite bands as the manifestation of energy changes.

It is a matter of interest to see to what extent these changes are limited to those of the oscillations of the atom within a group or to what extent they are shared by the rest of the molecule.

Much of this work of attempted correlation between bands and linkages has been done on liquids, and is considered elsewhere in this General Discussion, Lecomte, Henri, Bonino, Ellis, Smith, and Boord being workers in this field. It may be said, however, that associated with certain linkages, such as C—H, C—C, N—H, OH in primary, secondary, and tertiary alcohols and the benzene linkage, certain oscillation bands seem to be more or less characteristic, pointing to some degree of localisation in the infra-red spectrum from the visible up to 13μ.

Some examples of the factors to which weight has been given for these correlations may be briefly set down, the bulk of the evidence being derived from the study of liquids.

Repetition of bands or harmonic series of bands is found among the members of homologous series, as for example, the persistent occurrence of certain bands up to 14μ in the aliphatic hydrocarbons, and up to 10μ among primary alcohols.

Shift of a band has been observed on changing from a primary to a secondary, and thence to a tertiary alcohol, with the concomitant change of $CH_2OH \rightarrow CHOH \rightarrow COH$.

Identification of a linkage, for example C—H, with a band system has been inferred from the spectra of two such bodies as $CHCl_3$ and C_6H_6, which display between 1 and 3μ a number of bands in common.

Disappearance of a band concurrently with elimination of a group is

[35] *Activation et Structure des Molecules*, Paris, 1928, p. 96.
[36] R. T. Birge and H. Sponer, *Physical Rev.*, 1926, **28**, 259.

among the most cogent lines of argument in this work. Taking the N—H linkage as an example, Salant [37] found that when the hydrogen atoms of NH_3 were all substituted to give the (liquid) tertiary amine, a band at 3μ, which had up till then persisted in the mono- and diamines, suddenly disappeared. This band also occurs strongly in NH_3, and is considered [38] to be the first harmonic of the band of NH_3 (gas) at $6{\cdot}136\mu$. It is thus concluded that the degree of freedom which produces this band in NH_3 and the substituted ammonias so long as they contain one atom of hydrogen is peculiarly associated with the linking N—H. This question is also discussed in a paper by Ellis, to be read before this meeting.

In addition to the observations of coincidences and of the effect of suppression of bands in conjunction with changes in the chemical structure of the substance, attempts have been made to support the identification of a linkage with a band by comparing the calculated with the known value for some other constant, such as the heat of formation. An example of this is before this meeting in a paper by Ellis (p. 888), and other applications of infra-red data towards the elucidation of structure are mentioned by Rideal in a paper contributed to this Discussion.

It is not necessary here to do more than refer to the identification of certain bands given by solids with the groups NH_4^+, CO_3^{--} and SO_4^{--}.

(8) *Isotopes.*

A difference in wave-length in spectra that might be due to a difference in nuclear mass, the characteristic feature of isotopes, was sought for shortly after Aston's discovery, and faint indications were obtained in the ultra-violet by Merton and others. This was confirmed by Mulliken on various metallic compounds,[39] and later, through the co-operation of a group of investigators at the University of California and the Mount Wilson Observatory, have come a series of striking discoveries on the isotopes of oxygen and now of carbon,[40] reported to this meeting by Professor Birge, who discusses the theory underlying the spectroscopic data.

It was, however, from inspection of the infra-red spectrum of HCl (Imes),[41] that Loomis and Kratzer, in 1920, independently concluded from the doublets present on the rotation bands that the displacement was correct in magnitude and sign for two isotopes of the atomic weights 35 and 37, and moreover, the intensities were about right for isotopes of these atomic weights occurring in the proportion in which they do in ordinary chlorine.

(9) *Structural Models.*

For an account of molecular models, including the more or less polar molecules with which work in the infra-red has to do, the reader is referred to a communication by E. C. Kemble.[42]

A dumb-bell model is the simplest form, and that which no doubt represents the diatomic molecules, the hydrogen halides, CO, NO, and even C_2H_2. As has been indicated above the part played by the elec-

[37] *Proc. Nat. Acad. Sci.*, **12**, 72 (1926).
[38] Robertson and Fox, *loc. cit.*, p. 209.
[39] See Loomis, *Bull. Nat. Res. Coun.*, No. 57, **2**, 260 (1926).
[40] P. 718; and Patkowski and Curtis, on Isotopes in ICl, p. 725.
[41] *Loc. cit.*, and Colby, Meyer, and Bronk, *Astrophys. Jour.*, **57**, 7 (1923).
[42] *Bull. Nat. Res. Coun.*, No. 57, **2**, 293 (1926).

tronic momentum in this model is to produce the effect of a Q branch only if it is not in line with the vibrational axis; otherwise there is a missing branch in the resolved band.

There has been more discussion as to the nature of the model of triatomic molecules, such as H_2O, H_2S and CO_2. By taking into account the polarisation of the ions, Hund [43] considers the configuration of the molecules of H_2O, and H_2S as a system of points in equilibrium. For the stable form he deduces that the atoms of these two gases are at the corners of a triangle, the apical angle in the case of H_2S being sharper than that for H_2O. Rawlins, in a paper contributed to this [44] meeting, discusses the three possibilities of the gaseous CO_2 molecule having the models (*a*) of an isoceles triangle; (*b*) symmetrically linear; and (*c*) unsymmetrically linear. Having weighed analogies from X-ray work on solid CO_2, considered its molecular heat which has a value characteristic of diatomic gases, and taken into account the electric moment, Rawlins comes to the conclusion that the gaseous molecule of CO_2 is linear and symmetrical.

For NH_3 Hund, from a consideration of the polarisation and laws of force between the ions arrived at the conclusion that as soon as the polarisation reached the value where an equilibrium position was established, whereby the four ions formed a tetrahedron with three equal side faces, then this tetrahedron was stable. The existence of oscillation bands of various frequencies in the infra-red spectrum of NH_3 shows that the ions are separating and one of the modes of vibration may be considered to be the oscillation of *N* against the plane of the *H* atoms. In such a case, Hund's case will clearly be fulfilled, and a tetrahedral structure will be required for the model. Robertson and Fox [45] adduced, in support of this view, the large temperature coefficient of the dielectric constant of NH_3 according to Watson,[46] and accepted the view that the NH_3 molecule is tetrahedral, perhaps with the *N* at no great distance from the plane of the *H* atoms. They discussed the possible degrees of freedom of the atoms in the molecule, and endeavoured to associate some of them with the chemical linkage N—H. From their absorption spectra they considered that PH_3 and AsH_3 have a similar structure, but progressively the tetrahedra are becoming flatter.

The tetrahedral form of CH_4 with the carbon at the centroid and the hydrogens at the apices is deep-rooted in the history and experience of organic chemistry. It is accordingly satisfactory, in spite of some attempts to attribute to the molecule a pyramidal structure with carbon at the apex, that the bulk of the evidence from a consideration of spectra including the infra-red and other physical constants of the gas is in favour of the tetrahedral structure.[47]

(10) *Raman Effect in Gases.*

Although the investigation of modified lines scattered by liquids or vapours (the Raman effect) is so recent and the results for gases so scanty, nevertheless some very important conclusions have already been reached. Wood [48] has shown that gaseous HCl gives a modified line corresponding to the *Q* branch at 3·466μ, which is the exact position of the " missing "

[43] *Z. Physik*, **32**, 81 (1925).
[44] P. 925.
[45] *P.R.S.*, A. **120**, 207 (1928).
[46] *Ibid.*, 117, 43 (1927).
[47] Dennison, *Astrophys. J.*, **62**, 84 (1925).
[48] R. W. Wood, *Nature*, 1929, **123**, 299; *Phil. Mag.*, 1929, 7 (VII.), 744.

line in the infra-red absorption band examined by Imes. This missing line is the vibration transition of the nuclei when no charge of rotation occurs. It is peculiar that while no Raman line for CO_2 is found in the scattered spectrum for the bands at 2·7, 4·25 and 14·7μ, one is found for 4·64μ, where no CO_2 band is known. Rasetti [49] reports, however, that a pair of doublets may be observed giving difference of 1284 and 1392 cm.$^{-1}$, which are exactly those required for the difference between the components of the CO_2 infra-red band 2·70μ (*i.e.*, 2·67 and 2·75μ) and the band at 4·25μ. The fact that the 2·70 band is so closely connected with the 4·25μ band calls for further investigation, for in NH_3 gas the Raman line is that of 3μ, no line being found with gaseous NH_3 for the strong NH_3 bands at 6·1 and 10·55μ. Liquefied ammonia gas, however, is shown by Daure [50] to give a much more complex Raman spectrum. Daure finds three Raman lines, and these correspond closely with the position of the three centres of the triple-band observed by Robertson and Fox (*loc. cit.*) for NH_3 gas, while the 6·13μ band also has its counterpart nearly in this position in Daure's results. Wood (*loc. cit.*) has shown further that Raman lines for HCl gas correspond very well indeed with alternate lines of the rotation bands previously found by Czerny. It would seem that as regards gaseous substances, at all events, the effect arises from the utilisation by the vibrating molecule of a quantum of energy of infra-red frequency, with scattering of the remainder as modified radiation of longer wave-lengths. The "Anti-Stokes" lines would appear to arise from the molecule being excited to a higher energy level and scattering radiation equivalent to the energy of the exciting light to which is added one quantum corresponding to the infra-red frequency of the molecule.

(11) *General.*

The above constitute some of the principal services of infra-red research, so far as they have a bearing on molecular structure. The following lines of activity can scarcely be claimed to have this feature, but are mentioned to show the varied nature of the information that work in the infra-red region of the spectrum of gases can afford.

Thus, in the hands of Coblentz, infra-red data and technique have been used to determine the quantity of radiation from the sun, stars, and planets, and he has also deduced the temperatures which prevail in these bodies, and even the differences in radiation from the hemispheres of Mars.

As Garner and his school have shown in their work in which they favour the hypothesis of chemiluminesence rather than the thermal one for the emission of energy from flames, important deductions can be made as to the rôle of infra-red radiation in combustion, as, for example, in the effect of water, when it is present, in carrying off the energy of radiation produced when CO combines with oxygen; and as the bulk of the radiation from flames is in the invisible part of the spectrum and mainly in the infra-red, there is here a wide field of work in clearing up the mystery of flame, the same being true as regards the phenomena of explosion of both gaseous and solid explosives. Further, Paschen's determination of the emission and absorption bands of these gases is fundamental in questions relating to combustion.

The knowledge of the infra-red spectrum of water vapour and of CO_2

[49] F. Rasetti, *Nature*, 1929, **123**, 205. [50] This Discussion, p. 825.

is of importance in considering the nature and quality of energy reaching us from the sun, and only recently Dr. G. C. Simpson, by making use of the absorption coefficients of water and carbon dioxide in the infra-red, has deduced that an increase in solar radiation would result in increased cloud and precipitation and even in the apparent paradox of an ice age.

Future Work.

For its future development, it is felt that more attention should be given than has sometimes been done to infra-red technique. For example, scarcely enough attention has been paid to the calibration of the spectrometer and the temperature of the prisms ; failure to appreciate the importance of these might easily bring about a displacement of the order of the Kratzer correction.

The writer feels that not enough work has been done on the careful determination of this deviation from harmonic ratio. To trace a family of harmonics throughout a long range of frequencies may involve the setting and calibration of several prisms in the spectrometer, on the accuracy of which the identity with, or deviation from, harmonic ratio will depend. The necessity exists also for accuracy in fixing the position of oscillation bands when their wave-numbers are used for establishing the presence of presumed combination terms. The range of wave-numbers covered by a small difference in wave-length in the infra-red near the visible, is so great that a concordance with some combination of fundamental wave-numbers may have a fictitious appearance of exactness when set forth from the point of view of wave-length in μ.

By the use of gratings, numerous bands are now being resolved, and their fine structure due to rotation fringes dissected. There is no reason why the spacings between these fringes should not be obtained with sufficient accuracy for calculation, but, in addition, the centre of the band system should be checked by calibration of the instrument from some order of spectrum of a well-known line.

Perhaps it may be said that even for determining accurately the differences between oscillation bands, it is necessary in each case to have the fine structure, so that the true position of the centre portion of the band, with or without a Q branch, may be accurately known.

In the region between 17μ and 23μ, more exploration is wanted, both for the discovery of oscillation-rotation bands there, and also of rotation bands coming in from the farther infra-red.

As the question of intensity of the bands is assuming so much importance, the influence of instrumental conditions on intensity measurement requires attention.

Generally, it would be best to concentrate in the first place on the simpler gases, as the more complicated molecules present the greater difficulties.

There are many directions in which further work in the infra-red region should prove fruitful. Thus, more examples of the infra-red spectrum of matter in the three phases of gas, liquid and solid, would contribute to our knowledge of change of structure with physical condition.

More work on refractivity in this region is necessary in order to trace the dispersion curves and connect these with the dielectric constant at varying frequencies. Further work is also required to get an experimental basis for the constants of dispersion formulæ of gases.

It is found that absorption in the infra-red departs from Beer's law in some cases, obeying it in others; a correlation with work on gas compression should also prove interesting.

Already, from the Raman effect, important information is being obtained, and the explanation of Raman lines which do not correspond with infra-red bands and *vice versa* is likely to be of much value in settling the importance of bands with reference to fundamental frequency.

But it is impossible to indicate more than some of the directions likely to be taken by work in the infra-red region. The papers before this meeting show the trend of its usefulness in the solution of questions of molecular structure, and of its application to the general mechanics of the molecule and its constituent parts.

ON THE INFRA-RED SPECTRA OF GASES UNDER HIGH DISPERSION.

By Professor Ernest F. Barker and Professor Charles F. Meyer.

Received 7th June, 1929.

Investigation in the infra-red has developed without outstanding discovery, yet the total of improvement considered over a period of years is surprisingly great. For example, since the work of Ångström and Palmaer * in 1893, there has been a refinement which may be described as five-hundred fold. It is the purpose of the present paper to treat some of the later phases of the development which has taken place, and specifically those later phases with which the authors have intimate acquaintance. The discussion will be limited to an account of infra-red absorption spectra of gases as they have been studied where the authors have worked, at the University of Michigan. It is hoped that this restriction in scope will not be interpreted as a lack of appreciation for the work of others, or for other experimental methods. The method of investigation is characterised by the use of the diffraction grating. It will be briefly described, and some pertinent details regarding the equipment will be given. Typical results will be presented and their interpretation in terms of molecular mechanics will be reviewed. Finally, some suggestions will be offered in regard to the course along which further experimental development appears most promising.

Method of Investigation.

The gas is introduced into a cell,† C, Fig. 1, which is provided with windows of rocksalt or mica. Radiant energy from a Nernst glower, N, falls upon a concave mirror M_1, and is thereupon brought to a focus within the cell. It then falls upon the mirror M_2 and is focussed upon the slit S_1 of a monochromator, which consists further of the mirror M_3, a prism, P, usually of rocksalt, and a mirror M_4. A shutter is placed at the slit S_1. The monochromator produces a spectrum of low dispersion

* *Ofv. af Kongl. Vet.-Akad. Förh.*, **50**, 6, 389, 1893.

† In investigating the atmospheric gases water vapour and carbon dioxide, the cell is sometimes dispensed with.

of which a limited region, in the infra-red, passes through the slit S_2. This region is not narrowly limited, but comprises a rather wide range of wave-lengths, which is selected by setting the monochromator. The selected radiation falls upon the large concave mirror M_5, is rendered parallel and directed toward the grating G, where it is diffracted with high dispersion. A portion of the diffracted beam of the first order is directed back toward the mirror M_5, thence toward the plane mirror M_6, and toward the slit S_3. Here, by turning the grating, an ultimate narrow range of wave-length is selected for measurement. The position of the grating is read on the divided circle L. From the slit S_3 the radiation passes to the mirror M_7 and is focussed, through a rocksalt window, upon the junctions of a thermopile, T, which is connected to a galvanometer. The above described optical system is typical. Variations of detail have existed in various instruments some of which are of importance from the point of view of efficiency. The application of this type of double spectrometer to the study of absorption spectra of gases was originated by Professor H. M. Randall.

The function of the monochromator is to select energy of a given range of wave-length and to inhibit the passage of energy of one-half of this range, or one-third, or one-fourth, etc. Without the monochromator,

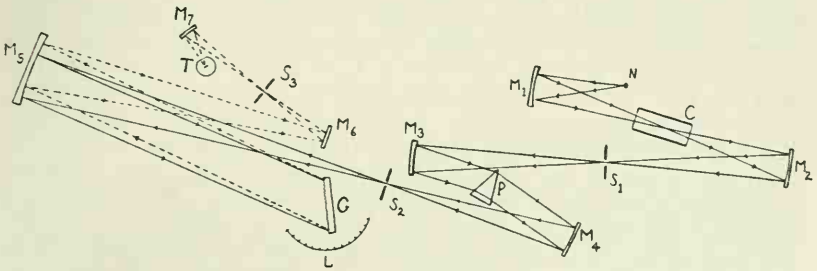

Fig. 1.—Optical system of double spectrometer.

energy of these fractional ranges would be diffracted in spectra of the second and higher orders, and pass through the slit S_3 to the thermopile, vitiating all determinations of absorption percentages. The monochromator by limiting the spectral range, greatly reduces the sum total of energy entering the grating spectrometer. It thus also lessens the danger of contaminating the spectrum by radiation scattered diffusely at the surfaces of the mirrors M_5 and M_6, and at the surface of the grating. The danger from diffuse radiation should be considered in any spectrometer, and especially when the energy in the spectrum varies greatly with wave-length. Then, while the instrument is used for measurements in the less favourable regions, the relative effect of diffuse radiation may be considerable.

To determine the absorption spectrum of a gas, the grating is set at regular intervals of arc, as indicated by the divided circle. At each setting the energy is determined by opening and closing the shutter, first with the absorption cell in the beam, and then with the cell removed from it. The percentage of absorption is readily deduced,* and this is plotted against settings of the circle. From the resulting graph of the spectrum, the positions of the absorption maxima are ascertained in

* The diminution of energy due to the windows of the cell is determined by subsidiary observations and taken into account, or compensating windows are used.

terms of corresponding circle settings. (These maxima are usually individual lines which constitute the so-called *fine structure* of a band.) The circle setting corresponding to each maximum may be translated by a previously-determined calibration into a wave-length * or wave-number. The calibration is made upon a known spectrum line,usually the mercury line at 1·04μ.

Some details regarding the optical apparatus and the receiving system may be of interest :—

In the earlier instruments † the focal length of the grating spectrometer was 0·5 m. In these the thermopile was placed immediately behind the exit slit S_3, and the mirror M_7 was not used. In a more recent larger instrument, which has proved itself very effective, the focal length is 1 m., and the mirror M_7 has been used for the first time.

The gratings are usually ruled on pure metals which are selected for their homogeneity. Alloys have been less frequently used. The final choice of metal depends upon the required spacing of the lines. When this is to be large, the groove should be deep, and the metal should be soft. In extending the use of gratings beyond 2 or 3 μ the necessity for relatively coarse ruling and for the greatest attainable concentration of energy is encountered. Smooth V-shaped grooves are obtained only by ruling with diamonds which have been properly ground and polished. Nickel is almost ideal as a metal for gratings of about 2000 lines per cm. ; one such grating has been obtained which is very effective between 3 and 5 μ. Aluminium gratings with about 1100 lines per cm. are effective from 5 to 9 μ. The nickel surfaces and the aluminium ones are optically polished preparatory to ruling. Pure tin is well adapted for gratings with not more than 800 lines per cm. The tin surfaces are prepared by cutting with a steel tool mounted on the ruling machine, with the same linear steps which are to be used in ruling. Gratings on tin have been used for observations to 14·8 μ. This limit is probably set by the diminishing energy of the beam and the increasing opacity of the rocksalt of the prism and the carbon dioxide of the atmosphere, rather than by the grating. The surfaces of the gratings are usually about 12 × 18 cm.

In the earlier spectrometers, compensated linear thermopiles of from ten to fifteen junctions in air were employed. These were usually of silver-bismuth, several by Randall, and one by Coblentz. They were used in conjunction with Paschen astatic galvanometers or with Leeds and Northrup high sensitivity D'Arsonval galvanometers. In the recent large spectrometer, a single compensated couple in vacuum was at first used. This was made of cast strips of the Hutchins alloys, according to the method of Pfund.‡ When it failed after doing valuable service, an uncompensated vacuum pile of two junctions was substituted. These two systems in vacuum were made by one of the writers. In work on the second one, a method of making the junctions, which has not been described to our knowledge, was found effective. Two small pieces of plate glass of equal thickness are laid on a flat surface. The strips which are to be joined are laid, one on each piece of glass, with one end projecting three or four millimeters over the edge of the glass. The other end is held down with a light object and a minute amount of a solution of solder

* For details see No. 16 in table of references.

† Those used by various investigators for researches published between 1918 and 1925.

‡ A. H. Pfund, *Physikal. Z.*, 13, 870, 1912.

paste in gasoline is applied to the free end. The two strips are now lined up and brought into contact while viewing them under a low power microscope. A loop of nichrome wire electrically heated to low redness is brought down toward the junction from above but without touching it. The ends of the strips fuse due to the heat radiated from the loop and weld firmly together. The process must be watched through the microscope. The advantage of having the ends of the strips project over the edges of the pieces of glass and making the junction *in air* and not *on* a plate of glass is twofold: Fusion can be readily brought about by the heat radiated from the loop, and this cannot be done when the strips lie on a plate of glass or other material, on account of cooling by conduction. Further, the sticking of the junction to the plate, which ordinarily results from the soldering or welding, is obviated. Bismuth solder may be used in making the junctions, but they can also be made without solder. The receiving areas are now soldered or welded to the junction, also by heat radiated from the nichrome loop. In this process the junction remains midway between the two pieces of glass *in air*. The original weld will not part unless the heating is carried too far. Fine copper leading in wires are attached in the same manner.

A Moll thermo-relay has proved itself extremely valuable. The recent improvements in apparatus and technique have brought about a fourfold refinement of measurement, and an extension of the spectral range which is easily accessible, from 8μ to nearly 15μ.

Typical Results and their Interpretation.

The absorption bands lying in the near infra-red arise from changes in energy of vibration and rotation. They are of interest principally because the unexcited state of the molecule is involved. Relatively few electronic bands yield information concerning the normal state, and they usually lie in the extreme ultra-violet where high dispersion is not available. The pure vibration bands have less variety than do those in which electronic transitions occur, since fewer degrees of freedom are involved. This is, generally speaking, an advantage. There are also disadvantages, however, since methods of observation are somewhat less precise, and combination relations are few because extended sequences of bands are rarely observed.

Those gases for which vibration bands have been resolved appear in the accompanying table, where they are listed in four groups in the order of complexity of the rotation. The first group includes the diatomic molecules, and two others whose structures are linear or nearly so. Since, for such systems, two of the principal moments of inertia are equal and the third is vanishingly small, the rotating nuclei move only in a plane. No rotation about the axis of figure occurs because the requisite quantum of energy is too great, rotational quanta being inversely proportional to the moment of inertia involved. Methane, which stands alone in the second group, occupies this unique position because its ellipsoid of inertia is probably a sphere. It may rotate about any axis without precession. In the third group are the molecules which rotate with a simple procession. They have two equal moments of inertia, and a third which may be either larger or smaller. The last group consists of a few representatives of that very large class with three unequal moments of inertia.

TABLE

Classification of molecules into groups according to nature of rotation. Groups are indicated by Roman numerals; Arabic numerals indicate references.

I. HF, 1.
HCl, 1, 2, 3, 4, 5, 6, 7, 8.
HBr, 1
CO_2, 9.
C_2H_2, 10.

II. CH_4, 11, 12.

III. CH_3F, CH_3Cl, CH_3Br, CH_3I, 13.
NH_3, 14, 15.
C_2H_6, 10.

IV. H_2O, 16, 17.
H_2S, 18.
C_2H_4, 10.

The character of the absorption bands depends upon the nature of the rotation and upon the direction within the vibrating molecule of the change in electric moment. In a diatomic molecule the electric moment may vibrate only along the line joining the nuclei, and, if the electron shell has no resultant angular momentum, the axis of rotation must be perpendicular to this line. As a consequence the bands consist of P and R branches only, with one line missing at the center. A well-known example is hydrogen chloride. Its fundamental band, lying near $3{\cdot}5\mu$, is shown in figure 2*a*, as mapped by Randall and Imes.* This band has

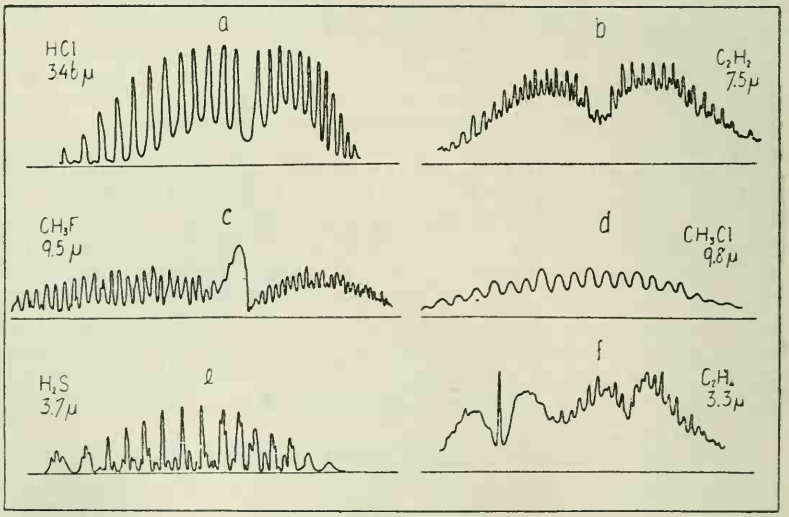

FIG. 2.—Typical bands.

been re-measured several times with great care. A portion of the R branch as recently determined is shown in Fig. 3*b*. Here the doubling of each line due to the two isotopes of chlorine is completely revealed. By comparing the formulæ for the frequencies of the lines due to HCl_{35} and HCl_{37} it is possible to show that the two isotopic forms are identical as to dimensions and fields of force, the doubling being a mass effect only.

The second band shown, Fig. 2*b*, is due to one of the fundamental vibrations of acetylene, and shows a somewhat similar structure. It lies at about $7{\cdot}5\mu$. The absence of a Q branch shows that the vibration

* See table for complete reference.

is normal to the axis of total angular momentum. Hence there can be no precession, and the configuration must be practically linear. Another acetylene band, at about 13·5μ, has a strong Q branch. It must arise from a vibration perpendicular to the line joining the atoms, *i.e.*, parallel to the axis of rotation. Both of these bands exhibit a striking alternation in the intensities of the component lines, which is a further indication that only plane rotation is involved. The differences in intensity are a consequence of the nuclear spin of the hydrogen atoms, which results in a division of the C_2H_2 molecules into two classes. The spin vectors are all parallel to the axis of rotation, but in some molecules both are in the same sense while in others they are oppositely directed. A rotation of 180° leaves the former system unchanged, and such molecules are distributed only upon alternate levels in the energy diagram. The latter must turn 360° to complete a period, and they occupy every level. Thus the rotation states have alternately larger and smaller populations, which are reflected in the intensities of the corresponding lines.

The vibration spectra for gases included in group III. are similar in some respects to those of acetylene. Two types of bands are observed. The first, showing well-defined P, Q and R branches, is illustrated by the band of methyl fluoride at 9·5μ, Fig. 2*c*. It is associated with a vibration of the electric moment *parallel* to the axis of figure. The second consists of a continuous succession of absorption maxima with intensities which are greatest near the centre and diminish symmetrically toward either side. These maxima are, in fact, the Q branches associated with a family of bands successively displaced by almost equal frequency intervals; the lines of the P and R branches have a different spacing, and usually fall together into a nearly continuous background. This type arises from vibrations *perpendicular* to the axis of figure. The band due to methyl chloride at 9·8μ shown in Fig. 2*d* is an example. Every third line appears somewhat intensified as a result of a three-fold symmetry in the arrangement of hydrogen nuclei. Ammonia exhibits this same characteristic in the bands lying near 2μ and 6·5μ.

The rotations of the molecules for the gases of group III. correspond to the motion of a symmetrical top, and involve two different moments of inertia. There is an angular momentum $ih/2\pi$ about the axis of figure, with a simple precession of this axis about the invariant line. The latter is the axis of the total angular momentum $jh/2\pi$. The angle of precession varies from state to state ($\cos\theta = i/j$). Consequently, the directions of the fundamental vibrations can be neither parallel to nor perpendicular to the invariant line, and all bands must exhibit Q branches with transitions $\Delta j = 0$. The bands with the single Q branches appear when $\Delta i = 0$, that is, when the change in electric moment is parallel to the axis of i. This means a change in total angular momentum and in angle of precession with no change in angular momentum about the figure axis, which explains why the line intensities are not affected by the three-fold symmetry. The line spacing is $h/4\pi^2A$ as in the diatomic case, A being the value of the moment of inertia about any line perpendicular to the symmetry axis. A particularly interesting example of this type of absorption is the band of ammonia near 10μ, illustrated in Fig. 3*a*. It is a superposition of two characteristic patterns, the centres lying at 10·3μ and 10·7μ. The doubling is due to the fact that the nitrogen nucleus lies very close to the plane of the equilateral triangle formed by the three hydrogen nuclei, the molecule being a pyramid of very small altitude. Two equilibrium positions for the nitrogen nucleus exist, one on either

side of the plane of the hydrogen nuclei. If the work necessary to push the nitrogen nucleus into this plane were very great, then the vibration levels for each configuration would be independent and identical. Every level is double, corresponding to a symmetrical and an antisymmetrical solution of the wave-equation, but the energy associated with each of these solutions would be the same. However, when the equilibrium positions are not far apart, and the potential energy barrier between them is low, the pairs of solutions involve slightly different energies and the doubling of the levels becomes appreciable. Vibrational transitions are between states of opposite symmetry character. Since antisymmetric levels lie above the corresponding symmetric ones, more energy is required to lift the molecule from a lower symmetric to an upper antisymmetric level, than from a lower antisymmetric to an upper symmetric one. The former transition explains the 10·3μ band, and the latter the 10·7μ band. From the frequency difference between the two centres a rough estimate may be made of the altitude of the pyramid. Since the two-rotation series give the moment of inertia about a line perpendicular

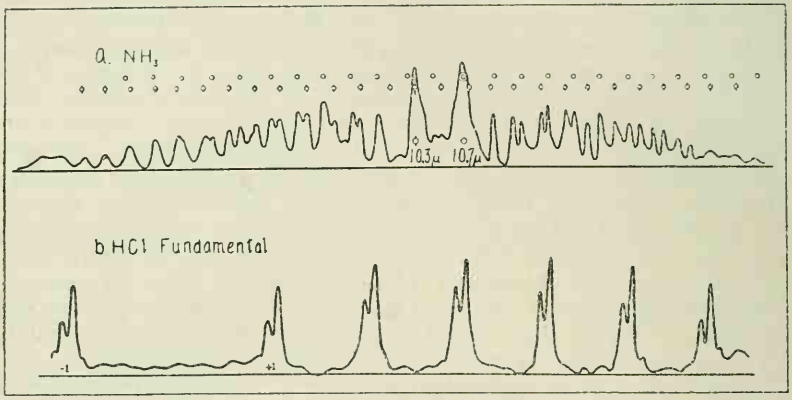

FIG. 3.—(*a*) The double band of ammonia. (*b*) Isotope effect in hydrogen chloride.

to the figure axis, the whole configuration may be computed approximately from measurements upon this one double band.

Transitions between vibration states in which the changes in electric moment are perpendicular to the axis of the molecule must always be accompanied by changes in the angular momentum about this axis ($\Delta i = \pm 1$). Since these vibrations may be resolved into components, both along the invariant line and normal to it, the bands will have P, Q and R branches ($\Delta j = 0$ or ± 1). The change in i without change in j is possible only when the angle of precession assumes a new value, requiring a change both in energy of precession and in energy of axial rotation. Hence the position of the component bands is different for each initial value of i and, as stated above, a succession of Q branches is observed. The frequency interval between Q branches would be $(1/C - 1/A)h/4\pi^2$ if the molecule were rigid, C being the moment of inertia about the symmetry axis. Apparently this spacing may be considerably modified, however, by some factor perhaps related to the coupling between rotation and vibration. Where two or more bands of this type have been observed for a given molecule the ratio of their frequency intervals is in each case considerable, and sometimes nearly 2 : 1. Con-

sequently, a precise value of C is not obtained. However, various bands of the other type associated with vibrations parallel to the axis consistently yield the same values for A.

Molecules having three moments of inertia, all different, yield absorption patterns which are considerably more intricate than those already discussed. There are some features in common, however. Water vapour is an outstanding example. Its spectrum has been observed in very great detail, but has not as yet been completely interpreted. Two types of bands may be recognised, one with a strong central Q branch and the other without. The form of the latter type is not the same for all substances, but depends upon the relative values of the three moments of inertia. When the distribution of mass is nearly linear the pattern appears very much like curve $2b$, though it arises from different transitions. The spacing interval is $h/4\pi^2C$, C being the smallest moment of inertia. Ethylene is apparently an example of the assymetric rotator with one very small moment of inertia. Curve (f) shows two partially resolved ethylene bands, one of each type, which happen to lie close together. When the mass distribution approaches more nearly that of a plane disc, the band has an appearance somewhat like curve (d). An example is the hydrogen sulphide band near $3{\cdot}7\mu$, curve (e). The spacing of the strongest lines depends only upon the largest moment of inertia. It has been possible by comparing this band with a second one of the other type, which occurs at $2{\cdot}6\mu$, to derive the values of all three moments of inertia for H_2S.

Suggestions for Experimental Development.

It is desirable that the spectra of many additional gases should be studied under high dispersion, and it is probable that the spectra of many liquids and solids should be likewise studied. The future thus presents the challenge of planning for the investigation of a wide field in great detail. Were an improved instrument to be constructed for such investigation it would probably embody the following general features :

The focal length should be greater than that of present instruments. Doubling the focal length would, for a given size of grating, decrease the angular aperture of the beam by a factor of four. By way of compensation the slit width* could be doubled without increasing the spectral range included by it above the present range. The received energy may be considered to vary as the square of the slit width, and there would thus be neither loss nor gain in the energy. However, reduction of the angular aperture and widening the slits would facilitate the design and operation of the instrument.

There is hope that larger gratings may be ruled in the future, and their power of concentration may possibly be increased.

The monochromator should be provided with a prism of rocksalt, and interchangeably with one of sylvin to permit measurements between 15μ and 20μ.

Water vapour and carbon dioxide should be removed from the path of the beam. This might perhaps be accomplished by successive rough evacuations of the instrument and refilling with air from which these constituents have been removed.

The large mirror of the grating spectrometer should be figured to give

* This refers to the widths of slits S_2 and S_3 which are equal.

a truly parallel beam, instead of having a spherical figure as in present instruments, from which some astigmatism results. If the optical arrangement of Fig. 1 were adhered to, the mirror would have to be parabolic, with the axis of the parabola lying six or eight centimeters beyond the periphery of the mirror. The aperture should be 30 or 40 cm. and the making of such a mirror would present a difficult problem to the optical manufacturer. An alternative optical arrangement would be to put slits S_2 and S_3 (Fig. 1) in front of the grating and use an ordinary parabolic mirror. Reflections at small mirrors placed very close to the slits would be necessary.

Automatic recording has from time to time been carefully considered, but would probably not possess the advantages which might upon first thought be expected. It is believed that other methods should be looked to for the present in order to save labour and expedite investigation. Provision should be made to allow the equipment for automatic recording to be installed eventually, if this later proved desirable.

A hindrance to rapid work has thus far existed through the circumstance that it is necessary to employ several gratings of different constants to cover the near infra-red region satisfactorily. Frequent changes of gratings have, therefore, been necessary, each one involving adjustment and calibration. In the present spectrometer of 1 m. focal length, the mounting of two gratings of different constants, back to back, has been helpful. In an improved spectrometer, arrangement should be provided for installing permanently four or more gratings. They should all be adjusted upon installation. A simple manipulation should place any one of them in the optical beam, and further adjustment should be unnecessary. The gratings should be carefully calibrated, and graphical tables should be made by which circle settings can be converted into wave-length or wave-number without computation.

It might be possible to obviate the necessity of making two measurements of the energy at each setting of the grating. At present, one measurement is made with the absorption cell in the beam, and one is made with the cell removed. A contemplated scheme would make use of two cells and two beams, one passing through each cell. The gas under investigation would be placed in one cell, and the other cell would be empty. The two beams would eventually fall, one on each of the opposed junctions of a compensated thermocouple. If the gas did not absorb at the position in the spectrum for which the instrument was set, then the galvanometer would not deflect upon opening the shutter. If the gas did absorb, the deflection would be proportional to the amount of absorption. A method analogous to Pfund's method of double deflection might be used in conjunction with this arrangement. This method would consist in bringing about a rapid interchange in position of the two cells.

The task of constructing such a spectrometer and putting it into operation would be a great one, but were it once completed, the instrument should furnish a means of carrying out a precise and detailed study of numerous absorption spectra with relative rapidity.

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CHEMICAL STRUCTURE AND INFRA-RED ANALYSIS.

By Eric K. Rideal.

Received 1st August, 1929.

Up to quite recent times the interest in rotation and rotation vibration spectra of gases and vapours has been directed chiefly to securing positive information on the various energy levels obtainable on excitation so as to provide material for testing the validity of the analytical processes involved in the wave mechanics and in the selection principle. We are chiefly indebted to V. Henri [1] for drawing attention to the important chemical information available. Whilst the electronic structural symmetry of atomic ions and of diatomic ions of increasing valency as we move from group to group in the periodic system has been deduced from observation of the spectral systems especially by Fowler and Mulliken, the chemist is concerned chiefly with the properties of non-ionised molecules. Franck [2] has pointed out the importance of the determination of the convergence point of the vibrational spectrum for an interpretation of the mechanism of photo-chemical dissociation and for the evaluation of the dissociation energy effected by oscillation, whilst V. Henri has drawn attention to the possibility of dissociation by mere rotation and has made the important observation that in a number of bands with rising values of m, the quantised rotation as revealed by the fine structure suddenly disappears and is replaced by a continuous spectrum. Molecules, *e.g.*, S_2 and SO_2, HCHO in this state of excitation or " predissociated " are actually metastable and extremely chemically reactive.[3] A great deal of information may be obtained from an exact

[1] *Structure des Molécules*, 1925, *et seq.* [2] *Z. physik. Chem.*, **130**, 144, 926.
[3] Bonhoeffer and Farkas, *Z. physik. Chem.*, **134**, 337, 1927.

determination of the fundamental frequency ω_0. Thus, as Snow has pointed out, the data of Levin and Meyer on the spectrum of acetylene allow us to conclude with some certainty that the supposed tautomeric modification of acetylene $-C=CH_2$, if present at all, can exist only in extremely small quantities, and that the normal form is certainly a linear molecule HC : CH. In the same manner a solution to the vexed question of the tautomerisation of HCN and HNC might be found. Studies in the equilibrium and rate of attainment of equilibrium in tautomeric systems such as $CH_3 . COH . CH . CH_3$ and $CH_3 . CO . CH_2CH_3$ would probably be capable of resolution by this method.

For this purpose, however, it would be necessary to obtain accurate measure of the absorption coefficients of each form. Dependent both upon the evaluation of ω_0 and on intensities is the resolution of systems such as $Cl_{35}Cl_{37}$. The determination of the distribution of the three isotopic forms of molecular chlorine $Cl_{35}Cl_{35}$, $Cl_{35}Cl_{37}$, $Cl_{37}Cl_{37}$ presents one of the most interesting problems to be solved by this method, one, however, distinctly more difficult than that successfully achieved first of all partly by Imes and more recently by Levin and Meyer for hydrochloric acid gas. In more complex molecules the separation of the various moments of inertia from the analytical data presented by infra-red analysis has scarcely begun. It is probable that CO_2, O_3, H_2S, H_2O, present a series of molecules in gradation from the almost linear to the acute triangular.

The determination of the stability of these systems and a comparson with that determined from the potential functions of the binary systems, *e.g.*, for CO_2 the partial systems C—O and O—O presents interesting possibilities. We may observe, for example, that Mecke [4] identifies three of the complex band systems in the infra-red of water vapour as assignable to definite rotations :

(1) $\nu_1 = 24{\cdot}5\ m = \dfrac{h}{4\pi^2 I_1 m}$ ρ constant $m \rightarrow m - 1$.

(2) $\nu_2 = 16{\cdot}8\ (\rho + \frac{1}{2}) = \dfrac{h}{4\pi^2}\left(\dfrac{1}{I_2} - \dfrac{1}{I_1}\right)_{\rho+\frac{1}{2}}$ m constant $\rho \rightarrow \rho - 1$.

(3) $\nu_3 = 55{\cdot}5\ (r + \frac{1}{2}) = \dfrac{h}{4\pi^2 I_3}\ (r + \frac{1}{2})$; ρ constant, m constant, $r \rightarrow r - 1$.

With this assignment he obtains :—

$$I_1 = 2{\cdot}33\ 10^{-40}$$
$$I_2 = 1{\cdot}35\ 10^{-40}$$
$$I_3 = 0{\cdot}98\ 10^{-40}$$

Whilst Eucken,[5] with a somewhat different assignment, obtains

$$I_1 = 3{\cdot}2\ \ 10^{-40}$$
$$I_2 = 2{\cdot}25\ 10^{-40}$$
$$I_3 = 0{\cdot}98\ 10^{-40}$$

In both cases the identity $I_2 + I_3 = I_1$ is fulfilled.

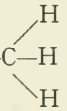
[4] *Bandenspektra, Fortschritte der Chemie*, 1929, p. 14.
[5] *Z. Elektrochem.*, **26**, 377, 1920.

With these moments of inertia it is, of course, possible to calculate the angle θ of the presumably symmetrical system since the mass of the oxygen and that of the two hydrogens are as 16 : 2 we obtain by resolution of the moments

$$\tan^2 \theta = \frac{8}{9} \quad \frac{I_2}{I_3}.$$

With Mecke's values $I/_2 I_3$ is either 1·35/0·98 or 0·98/1·35, giving angles of 47° and 42°, or with Eucken's values I_2/I_3 is either 2·25/0·98 or 0·98/2·25 giving angles of 32° and 55° respectively. It is difficult to decide between these values, but Debye [6] gives arguments from the electric moment of the water molecule for adopting the more acute form.

When the analysis of the work recently published in America on the infra-red spectrum of CH_3H, $CH_3 . CH_3$, CH_3Br, CH_3Cl and CH_3I is completed, it seems probable that the values of the moments of inertia for these molecules will permit of evaluation of the alteration of the tetrahedral angles of the carbon hydrogen of the



group as alterations are made in the group X. A commencement of the quantitative study of polarity can thus be effected by this method. Similar details may be forthcoming in the final analysis of the fine structure of the hydrides of the fifth group.

Recently much attention is being given, especially in America, by Bell and Ellis, to the identification of certain linkages in organic compounds by their characteristic infra-red absorption spectrum. In general terms the linkages —C—H, —C—X, —N—H and —S—H, are shown to possess a fairly definite spectrum. With sufficiently refined technique, some information on the alteration of polarity by substitution and the potential functions of these groups might be obtained. We may note that the mere identification of a number of these lines especially with the object of obtaining the fundamental frequency ω_0 may be obtained most readily and without elaborate apparatus by Raman's method.

The two fundamental constants ω_0 and I which are capable of being determined by infra-red methods can reveal as we have noted, a great deal of interesting information about the molecule. Some further information is immediately obtainable from a knowledge of the fundamental and of the overtone. Since the vibration frequency of the fundamental and of the overtone are given by $\omega_1 = \omega_0(1 - x)$ and $\omega_2 = 2\omega_0(1 - 2x)$ the values of ω_0 and of x are immediately obtainable. The importance of x as the measure of the anharmony of the vibrational movement of the linkage first indicated by Kratzer,[7] who determined the complete potential function for HCl from the data presented by Imes. A somewhat simpler method proposed by Mecke [8] consists in considering the dipole system as a function of two terms only, an attractive and a repulsive, writing for the potential

$$V = e^2\left(\frac{C_1}{r^p} - \frac{C_2}{r^q}\right).$$

[6] *Polar Molecules*, p. 73.
[7] *Z. Physik*, **31**, 289, 1920.
[8] *Ibid.*, **42**, 390, 1927.

The attractive law is assumed to be the Coulomb law of attraction, and the value of the exponent for the repulsive force, determined in solids from their compressibilities may be evaluated from the anharmony of the vibrator by means of the expression

$$\omega_0 x = \frac{B}{24}(2q^2 + 19q + 26),$$

where

$$B = \frac{h}{8\pi^2 IC} = \frac{27{\cdot}710^{-40}}{I}.$$

In Table I. I have collected the published values of ω_0 and of $\omega_0 x$

TABLE I.

Gas.	ω_0 Wave Numbers.	$\omega_0 x$ Wave Numbers.	$I_0 \times 10^{40}$	q.	Remarks on $\omega_0 x$.
HF	4003	41	1·345	1·02	Calc by Czerny.
HCl	2941	53·6	2·656	3·68	Expt. determined.
HBr	2590	31	3·314	2·59	,, ,,
HI	2272	Not known.	4·309	—	—
NO	1892	10	16·4	4·90	Expt. determined.
		13 from u.v.	16·4	5·38	
CO	2155	11	15·0	3·82	,, ,,

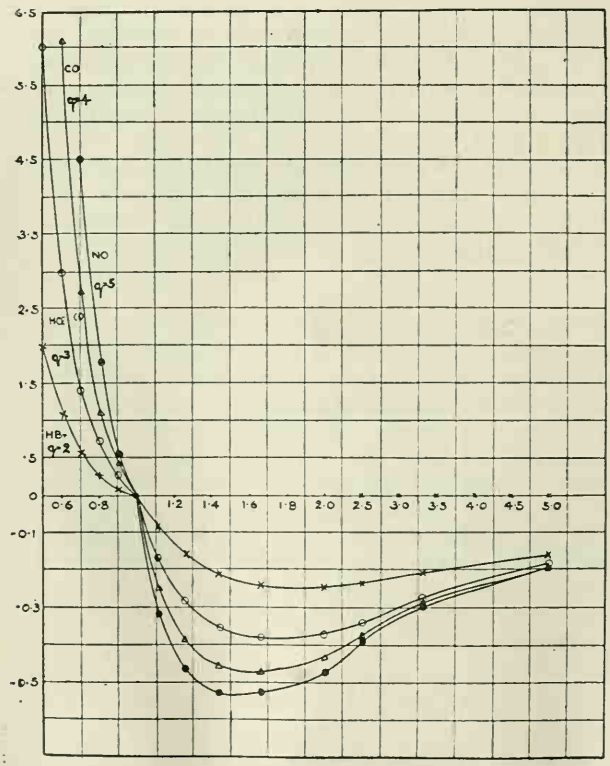


FIG. 1.

and I_0 and have calculated the values of the exponent for the repulsive forces.

It will be noted that the data for $\omega_0 x$ for HF must be regarded with some suspicion, probably the exact determination in the very near infra-red portion of the spectrum has proved rather a formidable task. We note that increasing deformability in the sense of the term employed by Fajans is accompanied by a fall in the value of the exponent, thus Br in HBr is more deformable than Cl in HCl. Carbon monoxide is distinctly more

deformable than nitric oxide. The information thus provided appears to be valuable, and we obtain another method in addition to the methods applied to salts such as the refractive index of the free gaseous ions (Fajans) the interionic distance in the crystal lattice, the lattice energy, solubility and photo-electric conductivity of solids.

The various types of potential curves for excited molecules have been discussed in some detail by V. Henri, and especially by Franck.

I append in Fig. 1 a few curves derived from the potential functions given above and insert the respective potential exponents for the gases with the exception of HF.

Finally, I would like to allude to one other interesting phenomenon, namely, the broadening of the spectral lines on increase of pressure of the gas. It has long been thought that both the Stark effect and a kinetic gas effect are important. In the case of Paton's measurements of the vibration rotation spectrum for HCl over a range of temperature, the effective molecular target area or nearest distance of approach without the phenomenon termed by Perrin of isochronous induction taking place, appears to be over sixteen times the actual internuclear distance. Not only does an increase of pressure, but the addition of different gases exerts specific effects on the vibration rotation spectrum of a gas, thus presenting a phenomenon which may be similar to the relative efficiencies of different gases in quenching of fluorescence of excited atoms and molecules.

THE FORM OF THE MOLECULE OF CARBON DIOXIDE.

By F. I. G. Rawlins.

Received 4th June, 1929.

There is a choice of three possible models for the (CO_2) * molecule :— The last-mentioned, according to Hund,[1] is unstable, and therefore one

(*a*) The isoceles triangular.

(*b*) The symmetrical linear.

(*c*) The unsymmetrical linear.

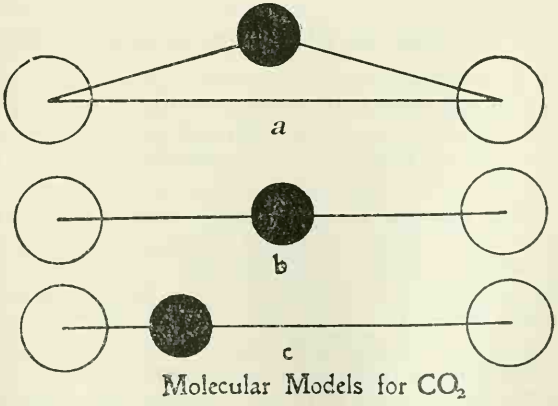


Fig. 1.

* An extension of the notation in favour on the Continent will be used. Thus brackets ( ) denote the gasous phase, { } the liquid, and [ ] the solid.

[1] Hund, *Z. Physik.*, 1925, **31**, 81.

is left with the two symmetrical forms to consider. This note attempts a discussion of the evidence, especially that of infra-red band spectra, for and against both of these. Apart altogether from the intrinsic interest of the problem, this gas forms an almost ideal illustration of the way in which molecular spectra, investigations on dipole moments and the specific heat can all be combined to lead to information which may now be accepted with some confidence as a discriminant between the alternatives (*a*) and (*b*).

1. The Transition Solid → Gas.

$[CO_2]$ possesses a characteristic molecular lattice, the units of which are the triatomic molecule itself with four to the unit cell.[2] Schæfer and Philipps [3] argue that because X-ray evidence indicates a linear arrangement for the molecule this is no reason why the gas should necessarily have the same (linear) form. Unfortunately observations are as yet too few to stress this point, especially since modern work on polymorphism has revealed the fact that a number of substances pass through a change of form a few degrees below their melting-point. All thermal considerations, particularly those involving density, depend upon being absolutely certain which form—supposing polymorphy—of the solid it is that melts, or in this case, sublimes. Examples are well known in which atomic environment is conserved through the act of sublimation, while others occur in which the symmetry of the unit decreases for change of state.[4]

Reasoning purely by analogy, one would expect that, whatever arrangement was stable at the melting-point, it would be that of the gas (perhaps strictly only in such a temperature range for which the "characteristic temperature" of Debye is large compared with the absolute temperature considered). Such a view seems reasonable for molecular lattices, for in these the inter-molecular binding is far weaker than the forces acting within the molecule itself. Whatever happens, polarisation must tend to decrease the intra-molecular nuclear separation in the process $[CO_2] \rightarrow (CO_2)$, and this is in itself more compatible with the persistence of the linear form than with a change to a triangular one.

2. Infra-red Absorption Spectra and Molecular Heats.

It is well established that there are three regions of selective absorption in the infra-red spectrum of (CO_2), lying at approximately $2{\cdot}72\mu$ $4{\cdot}25\mu$, and $14{\cdot}7\mu$. Models (*a*) and (*c*) require three frequencies and (*b*) two, so that *prima facie* the spectral evidence is in favour of (*a*), the unsymmetrical rod being excluded as already mentioned.

Schæfer and Philipps [3] maintained at the time when their work appeared that all three bands were to be regarded as fundamental modes of vibration of the (CO_2) complex. Conversely, Eucken [5] put forward the view that only the swings at $4{\cdot}25\mu$ (carbon vibrating along the join of the oxygens) and at $14{\cdot}7\mu$ (carbon vibrating perpendicularly to the join of the two oxygens) were fundamentals, whereas the $2{\cdot}72\mu$ band is a combination tone of that at $4{\cdot}25\mu$ together with an inactive oscillation of the two oxygens in phase along their join with respect to the carbon.

[2] Mark, *Z. Electrochem.*, 1925, **31**, 523.
[3] Schæfer and Philipps, *Z. Physik*, 1926, **36**, 641.
[4] Rawlins, *Trans. Faraday Soc.*, 1929, **25**, 283.
[5] Eucken, *Z. Physik*, 1926, **37**,714.

Eucken is here imagining model (*b*), and cites two facts in support of his contention. Firstly the intensity *I*. If the linear form is the true one, then obviously $I_{4\cdot25} > I_{2\cdot72}$; whereas the triangular model vibrating in the manner conceived by Schæfer and Philipps should give $I_{2\cdot72} > I_{4\cdot25}$. In the next section it will be seen how the former turns out to be correct. Meanwhile, it may be pointed out how uncertain most intensity measurements by direct observation in the infra-red may be when pressed into service as quantitative criteria. The present author may be permitted to speak from sad experience in past attempts in grappling with this difficulty. Progress has been made during the last year; it is just becoming possible to ascribe a real numerical value to observed intensities of absorption, to which Dennison's theoretical treatment [6] has provided an impetus. Unless, however, such experimental readings can be compared with a dispersion curve—as is the case for (CO_2)—it may prove meaningless to apply the more delicate analysis. Secondly, the Molecular Heat at constant volume C_v. For (CO_2), C_v tends to the value $5R/2$ at low temperatures, characteristic of diatomic gases. A triangular model would give $3R$, and thus the symmetrical rod is strongly indicated.

Another point, although not strictly independent, is that, on the assumption that (CO_2) is thermodynamically diatomic, excellent agreement results between the value of the moment of inertia calculated from Barker's work in the infra-red [7] and that deduced from the chemical constant.[8]

It is clear that classical thermodynamics could not be expected to offer a final solution of such a problem as that of molecular form. An interesting attempt by McCrea [9] based upon the new mechanics is suggestive in asking whether change of form could be brought about by the stimulation of a particular frequency at a certain temperature. The evidence to be discussed in the next section seems conclusive enough to warrant the abandonment of this ingenious hypothesis for the present, or at least until more is known about the relationship between absorption and temperature in gases.

3. The Electric Moment.

The index of refraction n of a gas is connected with its characteristic frequencies by an expression of the form

$$\frac{n^2-1}{n^2+2} \sim \frac{2}{3}(n-1) = \sum_i \frac{Ci}{\nu_i^2-\nu^2} = n(\nu, p_i) \quad . \quad . \quad (1)$$

where ν_i refers to any position of selective absorption (ν being taken as the independent variable), and C_i is a constant equal to $\frac{e^2N}{\pi m}p_i$ (e = charge, $N = 6{\cdot}06 \times 10^{23}$, m = mass), in which p_i represents, according to the classical theory, the number of resonators at the band of frequency ν_i or, on quantum grounds, the transition probability giving rise to such absorption.

A detailed experimental test of the function $n = n(\nu, p_i)$ for (CO_2) by

[6] Dennison, *Physical Rev.*, 1928, **31**, 503.
[7] Barker, *Astro. J.*, 1922, **55**, 391.
[8] Eucken, *Z. Physik*, 1924, **29**, 1.
[9] McCrea, *Proc. Camb. Phil. Soc.*, 1927, **23**, 890.

Fuchs [10] shows strong anomalous dispersion at $4{\cdot}25\mu$, with correspondingly large values of p_i. On the other hand, there is practically no anomaly at $2{\cdot}72\mu$, and the associated value of p_i is nearly zero there. From this very significant result it may be inferred that Eucken's assumption, leading to $I_{4\cdot 25} > I_{2\cdot 72}$ is substantially correct, and that the observed intensity at $2{\cdot}72\mu$ is too high.

Closely related to the refractive index is the molecular polarisation P defined by the equation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{M}{d} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ϵ is the dielectric constant, M the molecular weight, and d the density. P is a measure of the displacement of the electric charges by an external electric field, and should be independent of the temperature for molecules devoid of a permanent electric moment **p**. For molecules having a finite value of **p**, the total polarisation is made up of two parts yielding

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{M}{d} = \frac{a}{T} + b = \epsilon(\mathbf{p}, T) \quad . \quad . \quad . \quad (3)$$

where a contains **p**, and b does not involve the temperature T. Actually, $a = \frac{4\pi N \mathbf{p}^2}{9k}$, in which k is Boltzmann's constant. Plotting $T\epsilon(\mathbf{p}, T)$ with T as variable leads to a straight line intercepting the ordinate at a point which is a measure of a, while its slope indicates the contribution to P which is independent of the temperature, *i.e.*, the term b. This is in essence Debye's theory.[11]

A finite value of a thus provides an unassailable proof of the presence of a permanent electric moment. Unfortunately, however, the technique for the determination of ϵ with sufficient precision has waited long before reaching the very exacting needs of such work, but the recent attack by Stuart [12] leaves no room for doubt that the problem has been solved on the experimental side. The errors and uncertainties have been eliminated to a degree which permits a zero value for a to possess real significance. It is perhaps not superfluous to point out how refined Stuart's instrumental calculations are: for his immediate purpose, a negative result was far more important than a positive one.

Application to (CO_2) shows no intercept on the ordinate axis, leading definitely and conclusively to the linear symmetrical form, since the triangular model must inevitably possess a finite value for **p**, and therefore for a.

Stuart was also able to show that the electrostriction experiments undertaken by Kliefoth [13] when completely interpreted, result in the absence of a permanent moment in (CO_2).

Taking all the evidence into consideration, it can hardly be doubted that (CO_2) is linear and symmetrical, corresponding to the unit in [CO_2].

4. Stability.

As our knowledge of ionic and molecular deformability has increased, it has become patent how great, and sometimes overwhelming a part

[10] Fuchs, *Z. Physik*, 1928, **46**, 519.
[11] Debye, *Handbuch Rad.*, **6**.
[12] Stuart, *Z. Physik*, 1928, **47**, 457.
[13] Kliefoth, *Z. Physik*, 1926, **39**, 402.

this property plays in structural questions in all three states of matter. Actually, the theoretical discussion for (CO_2) by Hund [1] and Heisenberg [14] shows that the unsymmetrical rod as in model (*c*) would require for stability a greater degree of deformation than the isoceles triangle, and hence its reality is decidedly improbable. The form (*b*) deduced from observation is therefore that for which the deformation is least. That very considerable effects due to polarisation are nevertheless to be expected is manifest from the fact already mentioned that the crystal lattice of $[CO_2]$ is molecular.

5. Future Problems.

Such a common compound as carbon dioxide still offers attractions to the investigator. Thus, information on the following matters would be valuable :—

(I) The verification of Dennison's formulæ [6] connecting absolute intensity, mean free path, and areas under the infra-red absorption curves for (CO_2).

(II) Infra-red and X-ray analysis of $\{CO_2\}$.

(III) Infra-red Absorption Spectrum of $[CO_2]$, with special reference to the detection of allotropic changes.

[14] Heisenberg, *Z. Physik*, 1924, **26**, 196.

Cambridge.

A NOTE ON THE PROBABLE INFRA-RED SPECTRUM OF SULPHUR VAPOUR.

By Professor A. M. Taylor.

Received 27th August, 1929.

Some years ago, the author made measurements on the infra-red spectrum of sulphur [1] in the solid and liquid phases, and came to the conclusion that it was probably internal vibrations of a molecule S_{16}, which were responsible for the absorption. An attempt has now been made to measure the absorption of the vapour.

The apparatus used was a cell made of a brass cylinder of 4 cm. diameter, having a slot 2·5 cm. × 0·8 cm., cut axially through it. The slot was enlarged at the extremities to 3·5 cm. × 1·5 cm.; the inner and narrower portion of the slot was closed by rock salt windows at either end. These were held in place by a screwed-on flange and a packing made of asbestos paper loaded with silver chloride was used. The silver chloride at about 400° C. is a waxy solid, and this helped to make a good seal. The extremities of the slot were closed by a second pair of windows of rock salt, similarly fixed and sealed. The central space in the cell thus formed could be evacuated, and those between the two pairs of end plates could be filled with nitrogen. The cell was wound with a heating coil of nichrome wire, and lagged with asbestos paper. The winding was chiefly at the ends, so as to keep these, with

[1] Taylor and Rideal, *Proc. Roy. Soc.*, A. **115**, 589, 1927.

the enclosed nitrogen, at a temperature at least as high as that of the central space. By this means, condensation of sulphur on the rock salt plates was avoided. About 0·8 amperes at 200 volts maintained the temperature at about 380° C.

It had been hoped to make careful measurements of the intensity of absorption, but it was found too difficult to keep conditions constant sufficiently long to do this, the rock salt plates disintegrating very rapidly. At a second attempt, therefore, only the positions of the maxima of absorption were sought. The general course of the absorption curve is probably that sketched in the Figure. The lower part of the Figure shows, for comparison, the course of the absorption curve for crystalline sulphur.

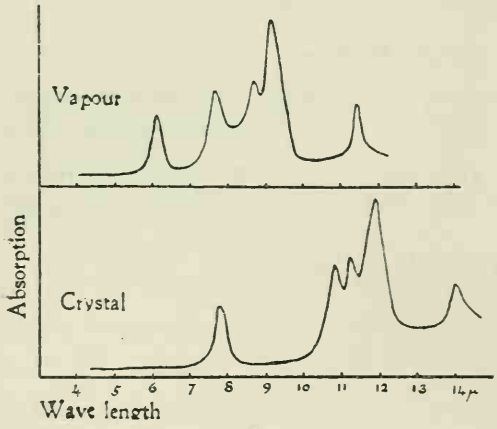


FIG. 1.

It is seen that the spectrum appears to be shifted towards higher frequencies, but to be otherwise of much the same character. The shift is the opposite way to that observed in raising the temperature of the solid or liquid states. If this shift is confirmed (it is at present uncertain by reason of the experimental difficulties encountered), it can only mean that constraints within the molecule are increased on passing into the vapour phase. (The molecule in the vapour is known to be S_8 or S_2 at high temperatures, and in the solid it was supposed to be S_{16}.) In the vapour phase, the molecule is no longer appreciably influenced by surrounding atoms, and it might be expected to contract. This would be likely to result in increasing the frequency of oscillation while preserving the general character of the whole spectrum. Further research on this would be very welcome.

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VIBRATION-ROTATION SPECTRA OF DIATOMIC MOLECULES.

BY C. P. SNOW (*Keddey Fletcher-Warr Student*).

Received 15th August, 1929.

There is now enough completeness about our knowledge of the vibration-rotation spectra of diatomic molecules to make a summary profitable. As absorption measurements form the only technique at present, it is possible to set a limit to the number of diatomic molecules

which can be considered (clearly only those which are stable under normal circumstances) ; and the experimental data upon their vibration-rotation spectra, and the theoretical interpretation, leave only a few gaps to be filled.

Vibration Bands.

The gross bands of the near infra-red, recognised early as caused by inter-nuclear vibrations, were shown by Kratzer [1] to be described exactly by the operation of the ordinary quantum conditions upon the energy expression for an oscillator

$$E = nh\omega_0(1 - nx \ . \ . \ .)$$

where ω_0 is the fundamental vibration frequency of the oscillator (and equal to $\frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$, where μ is the reduced mass of the oscillator, and K a constant which depends upon the inter-nuclear binding), and where x is a constant which represents the anharmonic nature of the oscillations.*

On the old quantum theory, n may be any whole number, but the new quantum mechanism introduces for it half-quantum numbers $\frac{1}{2}$, $\frac{3}{2}$. . . . Vibration-rotation spectra are inadequate to distinguish between the two forms.

For diatomic molecules there is only one possible ω_0, and, since the initial state of all transitions has $n'' = 0$ (on the modern theory, $n'' = \frac{1}{2}$) as the whole discussion is limited to absorption, the vibration band system is very simple. It becomes a fundamental with its centre at $\omega_0(1 - x)$ and overtones with centres at $2\omega_0(1 - 2x)$, $3\omega_0(1 - 3x)$, etc. The intensities of the overtones, which are weak compared with the fundamental, can be calculated to a first approximation from the fine structure of the fundamental by the use of the correspondence principle (Dennison).[2]

From the electronic band spectra ω_0 and x can be found, and when these are available the complete system of vibration bands can be predicted. The comparison of prediction and experimental fact is good where it can be tested (for NO and CO). It also follows that when ω_0 and x are determined from vibration bands determinations of heats of dissociation can be made with their aid, precisely as with the constants for electronic band spectra.

The other diatomic molecules whose spectra can be dealt with in absorption are the symmetrical molecules H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2, and the interhalogen compounds of the type ICl. It may also be possible to experiment on vapours such as S_2.

There is no doubt that the interhalogen compounds have vibration bands, but the heaviness of the molecules implies that they will lie beyond 20 μ (in fact, we know from electronic band spectra that ω_0 for ICl is 382 cm.$^{-1}$, *i.e.* c. 26 μ), and also that the resolution into rotational fine structure will be difficult. Hence they have not yet been reported, although from electronic band spectra their position and many characteristics for ICl, at least, may be inferred.

[1] Kratzer, *Z. Physik*, **3**, 289, 1920.

* The potential function for a harmonic oscillator is, of course, $V = kz^2$. For an anharmonic oscillator it becomes $V = kz^2 + k_2z^3 + k_3z^4$, z being the displacement of the nuclei. The molecular constant x, which is a measure of the anharmony, is a constant characteristic of the potential function. See Snow and Rideal, *Proc. Roy. Soc.* in publication.

[2] Dennison, *Phil. Mag.*, **1**, 195, 1926. The intensity ratio can now be calculated with greater accuracy from the quantum mechanical solution of a perturbed oscillator.

The known vibration band systems are in Table I :—

TABLE I.

Molecule.	Band System.
[3] HF	Fundamental : $\omega_0(1 - x)$ 3962 cm^{-1}. No overtones known.
[3] HCl	Fundamental : $\omega_0(1 - x)$ 2994 cm.$^{-1}$. Overtone : $2\omega_0(1 - 2x)$ 5667 cm.$^{-1}$.
[3] HBr	Fundamental : $\omega_0(1 - x)$ 2559 cm.$^{-1}$. Overtone : $2\omega_0(1 - 2x)$ reported by Brinsmade and Kemble,[4] but not resolved.
[5] HI	Fundamental : $\omega_0(1 - x)$, c. 2272 cm.$^{-1}$. Very weak and not resolved ; no overtone known.
CO	[6] Fundamental : $\omega_0(1 - x)$ 2144 cm.$^{-1}$. [6] Overtone : $2\omega_0(1 - 2x)$ 4266 cm.$^{-1}$. [7] Second overtone : $3\omega_0(1 - 3x)$, c. 6430 cm.$^{-1}$.
NO	[8] Fundamental : $\omega_0(1 - x)$ 1883 cm.$^{-1}$. [9] Overtone : $2\omega_0(1 - 2x)$ 3755, cm.$^{-1}$.

For the symmetrical molecule, however, there is practical certainty that there are no vibration bands ; the impossibility of this agrees with theoretical considerations of transition between symmetrical and anti-symmetrical, or odd and odd, states, considerations limited to these completely symmetrical molecules.

[It may be noticed as an unexplained fact that there is a small atmospheric absorption near the ω_0 of O_2 (1551) which appears to persist when the complete system is dried thoroughly.]

There is an interesting possibility for X_2 molecules, where the X_2 system contains isotopes. In any volume of chlorine, for example, there is an appreciable fraction of $Cl_{35} - Cl_{37}$ molecules. These molecules are not symmetrical, and the combination restrictions enforced upon $Cl_{35} - Cl_{35}$ are removed. That is, a vibration band of chlorine, due to the $Cl_{35} - Cl_{37}$ fraction, is to be expected in the neighbourhood of 555 cm.$^{-1}$ (ω_0 of Cl_2 from electronic data is 555 cm.$^{-1}$).

Rotational Fine Structure of Vibration Bands.

The partial analysis of the HCl band at 3·46 μ already obtained before 1916 was explained by Schwarzschild,[10] who found the quantum levels of a rotator to be expressed approximately by

$$E_r = Bm^2\left(B = \frac{h}{8\pi^2 I}\right).$$

[3] Imes, *Astrophys. Jour.*, **50**, 25, 1919.
[4] Brinsmade and Kemble, *Proc. Nat. Acad. Sci.*, **3**, 429, 1917.
[5] Czerny, *Z. Physik*, **44**, 235, 1927.
[6] Observed by several workers. The figures are recent values obtained in this laboratory.
[7] Schaefer and Thomas, *Z. Physik*, **12**, 330, 1923.
[8] Snow, Rawlins, and Rideal, *Proc. Roy. Soc.*, A. **124**, 453, 1929.
[9] Unpublished work, Snow and Rideal.
[10] Schwarzschild, *Sitzb. preuss. Akad. Wiss*, **1**, 548, 1916.

Later application of the Selection Principle ($\Delta m = \pm 1$, for the simple rotator) to transitions between such values of E_r gave an account of the fine structure of a vibration-rotation band,

$$\nu = \nu_0 \pm 2Bm$$

with the characteristic R ($+ 2Bm$) and P ($- 2Bm$) branches on each side of a zero line. Imes' work on the hydrogen halides confirmed the essential features of the theory; there was no Q branch ($\Delta m = 0$), and the lines near the centre of the band were approximately equally spaced. This spacing, which is $2B$, give a direct measurement of the moment of inertia I. There were, however, two difficulties. One was the apparent absence of the line $1 \rightarrow 0$; and the other was a convergence of the lines towards higher frequencies.

It is now convenient to distinguish between two types of molecules—S molecules, *i.e.* those which, like HCl, have $\sigma_e = 0$ (σ_e is the electronic orbital angular momentum parallel to the axis of figure. Its value is expressed by $S = 0$, $P = 1$, etc., by analogy with the l value in line spectra) and those which, like NO, have $\sigma_e \neq 0$.

For S molecules, when experimental data were to hand for HF, HCl, HBr, theory soon became consolidated, and has recently been confirmed for CO. The difficulty of the absence of the line $1 \rightarrow 0$ was at first surmounted by the assumption of half-quantum numbers in the energy formula. That is

$$E_r = B(m + \tfrac{1}{2})^2.$$

In 1926 Dennison [11] showed that for such molecules the eigenwerte from quantum mechanics are

$$E_r = Bm(m + 1)$$

where m is integral. This expression differs only by $\frac{B}{4}$, which is negligible, from the half-integral form above.

The convergence of the band lines was described quantitatively for HF, HCl, HBr by Kratzer, who used a more accurate energy formula:

$$E^n = E_0{}^n - m^2 a_n h + hB_0(m^2 - m^4u^2)$$

where

$$E_0{}^n = nh\omega_0[1 - (\tfrac{3}{2} + K)nu],$$
$$a_n = \tfrac{3}{2}nuB_0(1 + 2c_3),$$
$$u = \frac{2B_0}{\omega_0},$$

B_0 is the "rest" moment of inertia of the molecule,

$$K = \tfrac{15}{2}c_3 + \ldots$$

and c_3 is a constant of the potential function.

By finding a_1 from the measured positions of two corresponding lines in the R and P branches, the positions of the remainder of the lines of the fine structure can be calculated and compared with experiment. The agreement is very good in all the cases where the relation has been tested (HF, HCl, HBr, CO).

Recently another method has been proposed by Mecke.[12] He first

[11] Dennison, *Physical Rev.*, **23**, 318, 1926.
[12] Mecke, *Bandenspektra und ihre Bedeutung für die Chemie.*

expresses the potential function of the molecule in the suggestive form

$$V = -e^2\left(\frac{c_1}{r^p} + \frac{c_2}{r^q}\right)$$

where $$2\omega_0 x = B(\tfrac{1}{2}\tfrac{1}{2}pq - \tfrac{1}{6}(p-q)^2 + p + q + 1),$$

The bearing of these constants upon the internuclear forces is discussed by Dr. E. K. Rideal in another paper. Mecke uses them in the following energy expression for a vibrator-rotator

$$\frac{E}{h} = n\omega_0(1 - nx) + B_n m(m+1)[1 - u^2 m(m+1)]$$

where all the nomenclature has been defined except B_n, which is

$$B_0(1 - \alpha n) \text{ with } \alpha = \frac{2B_0}{\omega_0}(p+q).$$

The procedure in order to test the expression is much the same as for Kratzer's, for B_0 is taken from the separations of the first lines, and ω_0 and x are known from the positions of fundamental and overtone. In all the spectra mentioned before this method seems satisfactory; it would be interesting to try it on an overtone for which B, ω_0, x, were known from the fundamental, as then the positions of lines in it could be calculated completely from constants independent of measurements in the overtone itself. It is hoped to do this in this laboratory, possibly for the overtone of HBr.

The constants of the potential function follow from the convergence formulæ.* The use of these in relations based upon the correspondence principle led Dennison to a theoretical value of the relation of overtone to fundamental. The method is too long to be given here, but is discussed fully in the paper quoted above. A comparison of the theoretical values with the experimental is brought out in the table.

	Theor.	Obs.
HCl	·038	·05
HBr	·044	·06
CO	·032	·036

Better agreement has been attained by Meyer and Levin in their work on the HCl bands; they use the intensity ratio calculated upon the new mechanics. It is hoped to do this shortly for NO.

The intensity of individual rotation lines in any vibration band has been calculated by Hönl and London,[13] who arrived at the results:

$$(R)\ I(m, m+1) = B\left[\frac{(m+1)^2 - \sigma^2}{m+1}\right]$$

$$(Q)I(m, m) = B\left[\frac{(2m+1)\sigma^2}{m(m+1)}\right]$$

$$(P)I(m, m-1) = B\left[\frac{m^2 - \sigma^2}{m}\right].$$

The R, Q and P refer to the branches in absorption. The symbols have been defined before, except σ, which equals $\sigma_e \pm \sigma_s$.

In each case, of course, the value has to be multiplied by a Boltzmann

* See Kratzer, *loc. cit.*, and Snow and Rideal, *Proc. Roy. Soc.*, in publication where a fuller account is given.

[13] Hönl and London, *Z. Physik*, 33, 803, 1925.

factor. From these expressions, in S molecules, where $\sigma_s = 0$ and $\sigma_e = 0$, the Q branch is absent; this is an experimental fact. An attempt at the use of these theoretical relationships between the lines of a band has been made for the fundamental of CO; there are four lines whose measured intensity departs considerably from the calculated, but the agreement is not unsatisfactory when the difficulty of reliable intensity measurements is remembered.

Finally, the variation of intensity with temperature has been studied for one S molecule (HCl, by Colby, Meyer, and Bronk); [14] the broadening of the lines with pressure and addition of foreign gases, practically not at all; while the true shape of absorption lines in the vibration bands of these molecules has been revealed by Dennison and Bourgin.

For P molecules experimental data are much more scanty, and theory is correspondingly incomplete. There are naturally very few molecules in a P state under normal conditions, for an odd electron is necessary and carries with it great chemical reactivity. NO, in fact, seems to be the only P molecule which can be readily handled. For this molecule $\sigma_e = 1$, a necessary and sufficient condition for a Q branch, which has been observed. The energy expression $E_r = Bm(m + 1)$ is the same as for S molecules, with the substitution of half integral for integral quantum numbers [Dennison]. This has not yet been established by experiment.

	Character of Molecule from Vibration-rotation Spectra.	Molecular Constants.
HF	S	I and r, and the constants of Kratzer's potential function.
HCl	S	I, r, ω_0, x. Constants of potential function, both Kratzer's and Mecke's form. Heat of dissociation.
HBr	S	As for HF.
HI	Not established	Not established.
CO	S	As for HCl. Agreement with electronic data quantitative except for I, about which Asundi [15] has raised some doubt.
NO	$\sigma_e \neq 0$, *i.e.*, the molecule is P or D or . . . Indications of doublet state.	I, r, ω_0, x. Further inferences uncertain. Agreement with electronic data except for x, which is of the right order.

There is found experimentally less than the expected convergence and it may be that Kratzer and Mecke formulæ are not applicable to P molecules. The single line nature of the Q branch adds weight to the absence of convergence. On the other hand, the intensity of the overtone is only slightly less than that of the normal S molecule, CO.

While the S molecules exist, of course, in singlet states, the ground states of NO is a ^2P state. There may be a connection between the broadness of the tops of the bands in the fundamental of NO (the resolution

[14] Colby, Meyer, and Bronk, *Astrophys. Jour.*, **57**, 7, 1923.
[15] Asundi, *Proc. Roy. Soc.*, A. **124**.

applied to the overtone was not enough to effect more than partial resolution), and the superposition of the $^2P_1$ and $^2P_2$ states, the ω_0's of which differ by 0·4 cm.$^{-1}$.

This survey, intended as a sketch of the state of the subject, is completed by an attempt to represent in a convenient form the knowledge of diatomic molecules contributed by their vibration-rotation spectra, and the nature of the agreement of this knowledge with that obtained from electronic band spectra.

This note represents a stage in a formal scheme of work in which I took part at the invitation of Dr. Rideal, to whom I would pay here, as elsewhere, my sincere thanks. I am more than grateful to Sir Robert Robertson, for the most kindly and helpful encouragement throughout the work.

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Cambridge.

THE ABSORPTION SPECTRUM OF AMMONIA GAS IN THE NEAR INFRA-RED.

By Professor R. Mecke and R. M. Badger.

Received, 29th August, 1929.

The absorption of ammonia gas in the near infra-red has been investigated photographically under high dispersion with the use of a grating of 6·4 metres focus. It has been possible to photograph three separate bands of the oscillation rotation type with centres at about

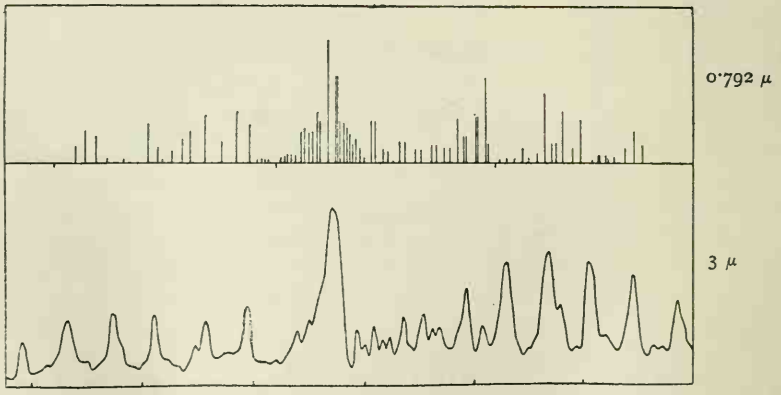


Fig. 1.

8810, 7920, and 6450 Å. respectively. We believe it is the first time that bands of this type have been investigated photographically.

The 7920 Å. band is the most intense of the three; it bears a strong resemblance to the 3μ ammonia band, of which it is apparently the third harmonic. Under the high dispersion employed, however, a complexity of structure has been revealed which would hardly be suspected from

the previous investigations on the ammonia bands made with thermocouples. Indeed, the complexity seems greater than that predicted by the simple theory of the symmetrical rotator.

On the basis of the quantum mechanics, the energy of such a rotator is expressed in terms of two quantum numbers by the familiar equation :

$$W = \frac{h^2}{8\pi^2}\left[\frac{1}{\mathcal{J}_1} j(j+1) - \left(\frac{1}{\mathcal{J}_1} - \frac{1}{\mathcal{J}_3}\right)m^2\right].$$

In the 7920 band we find a strong central line on either side of which are series of lines with a relatively small spacing and to be attributed to changes where $\Delta j = 0$, $\Delta m = \pm 1$. These series, however, appear to be double : which we attribute to a splitting up of the lines due to a slight dissymmetry in the molecule in the excited state, introduced by its rather great amplitude of vibration. Several series are present with the larger spacing, corresponding to changes where $\Delta j = \pm 1$ ($\Delta m = 0, \pm 1$). This spacing is the same as that found in the pure rotation spectrum. Within any series the convergence seems to be very small, but there are two kinds of series having very slightly different spacing : which seems a further indication of molecular dissymmetry. There are some evidences of alternating intensities, but the law does not seem to be a simple one. The band as a whole has a rather unsymmetrical appearance, as the branch on the short-wave side is both more intense and more developed.

An evaluation of the molecular constants from this band yields for the ammonia molecule : $\mathcal{J}_1 \approx \mathcal{J}_2 = 2{\cdot}78 \times 10^{-40}$ gm. cm.^{2} and $\mathcal{J}_3 = 3{\cdot}40 \times 10^{-40}$ gm. cm.^{2}, provided we assume the flat, rather than the acute pyramidal shape, which seems the more probable for several reasons. For the height of the pyramid we find $h = 0{\cdot}517 \times 10^{-8}$ cm. ; for the distance apart of the hydrogen atoms $d = 1{\cdot}43 \times 10^{-8}$ cm. ; for the distance N — H $r = 0{\cdot}977 \times 10^{-8}$ cm.

The band at 6450 Å. seems similar to the 7920 Å. band, and appears to be the fourth harmonic of the 3μ band. It was very weak, however, and requires further investigation with a greater depth of gas (5 metres). The band at 8810 Å. is of quite different nature, and seems to consist of simply two series of lines, displaced with respect to each other, both series having the same spacing. The spacing is such that we attribute this band to changes in which the two quantum numbers always have the same value, *i.e.*, $j = m$. This band seems similar to the band at 2μ, and we consider the two as analogous.

With the assistance of the new data, we have found it possible to explain all the known bands of ammonia as combinations of three fundamental frequencies, and their harmonics (unless the doubling of the band at 10μ can be taken as giving a fourth frequency). The fundamentals and their harmonics are given by :

$$\nu_1(n) = 3396n - 60n^2.$$
$$\nu_2(n) = 1630n.$$
$$\nu_3(n) = 966n.$$

The complete classification of the bands is given in the table on p. 938.

It will be observed that the combination frequencies are not the algebraic sums of the fundamental ones, indicating an appreciable energy of coupling. The first frequency $\nu_1 = 3336$ is to be attributed to the N—H bond of the ammonia molecule. It is now interesting to compare

λ.	ν.	Explanation.	λ.	ν.	Explanation.
10·35	966	ν_2	1·31	7640	$2\nu_1 + \nu_3$
6·13	1630	ν_2	1·20	8260	$2\nu_1 + \nu_2$
3·00	3336	ν_1	1·04	9650	$3\nu_1$
2·26	4420	$\nu_1 + \nu_3$	0·881	11350	$3\nu_1 + \nu_2$
1·98	5050	$\nu_1 + \nu_2$	0·792	12625	$4\nu_1$
1·66	6010	$\nu_1 + \nu_2 + \nu_3$	0·647	15440	$5\nu_1$
1·51	6610	$2\nu_1$			

the analogous frequencies of the polyatomic molecules CH_4, NH_3, OH_2, with those of the diatomic CH, NH, OH and FH. We see that the slight *increase* of the bond corresponds to a decrease of the nuclear distance r.

$X-H_n$.	ν_1.	r.	X – H.	ν_1.	r.
CH_4	3019	$1{\cdot}08 \cdot 10^{-8}$	CH	2800	$1{\cdot}13 \cdot 10^{-8}$
NH_3	3336	0·98	NH	3085	1·07
OH_2	3750	0·88	OH	3570	0·96
FH_1	3962	0·92	FH	3962	0·92

The absorption bands of arsine and phosphine investigated by Robertson and Fox are amenable to a completely analogous classification.

Physical Laboratory of the University,
Bonn.

GENERAL DISCUSSION

On Papers in Part III.

THE INFRA RED.

Professor Grimm (*Ludwigshafen*), said: With regard to Professor Taylor's paper (see p. 860), I would suggest that the infra-red spectra of the MnO_4' ion should be investigated not only in the crystallised or dissolved state but also in the form of crystals mixed with $BaSO_4$. With the assistance of G. Wagner and Cl. Peters it was possible to obtain mixed crystals of $BaSO_4 + KMnO_4$ with contents of permanganate up to 80 per cent. Furthermore, it would be interesting to compare in the mixed crystals of $BaSO_4$ and $BaMnO_4$ (which, strange to say, are violet) the state of the divalent MnO_4'' with that of the same but green coloured ion in solution. The mixed crystals of $BaSO_4 + KClO_4$ on the one hand with $BaMnO_4$ and on the other hand with $KClO_4$ may also be compared.

In this connection I should like to propose, in comparing K_2SO_4, K_2CrO_4 with $KClO_4$ $KMnO_4$, also to take $BaSO_4$ and $BaCrO_4$ into consideration, because then (*e.g.*, in the case of $BaSO_4$ and $KClO_4$), comparison is made of substances of the same type of structure MXO_4, with the same crystal gratings and with similar grating-spaces, just as Professor Schaefer has done with $CaCO_3$ and $NaNO_3$.

Professor E. F. Barker (*Michigan*), said: It is very common to associate a given vibration frequency common to several compounds with a particular chemical bond, or even with a certain pair of atoms within the molecule. Often this seems to be quite misleading. The force field surrounding each atom in a polyatomic molecule is far from isotropic, and depends, not only upon the equilibrium positions, but also upon the displacements of all the other atoms. The frequency of vibration of an atom, therefore, depends upon how it is displaced, and a *normal* vibration for the molecule is one in which all atoms oscillate with the same frequency.

In the case of NH_3, for example, the N atom may oscillate along the axis of symmetry, while the three H atoms approach and recede symmetrically. It is not at once obvious why such a motion should be ascribed to the N—H bond, nor why it should be associated with vibrations in other molecules whose constitution is very different.

I wish also to call attention once more to the danger of correlating the various bands for any substance such as ammonia, into series of fundamental and harmonic vibrations until the nature of the oscillation producing each band is known. The band at 2μ, for instance, in which the vibration is normal to the symmetry axis of the molecule, can hardly be an overtone of a band whose vibration is along the axis, nor even a combination frequency involving such a band. Analysis with sufficient resolution to reveal the true character of the vibrations is required before the fundamental frequencies and the combination relation may be discussed with confidence.

Sir Robert Robertson (*London*), in opening the discussion on infra-red spectra of gases, said he would take advantage of the President's suggestion to put forward questions that would invite discussion. He suggested that the interpretation of the infra-red bands of the ammonia spectrum was such a subject.

In addition to the work by himself and Dr. Fox, Professors Barker and Meyer, Mr. Ellis and Dr. Mecke, with Dr. Badger, had all concerned themselves with this spectrum, and these workers had contributed papers to this General Discussion, Barker having used a grating and Ellis and Mecke photography in the near infra-red.

The first point he raised was as to what are the fundamental frequencies.

Dr. Fox and he had avoided suggesting combinations of frequency to account for certain bands which did not lie in a harmonic series, such as those at 2·264 μ, and 10·55 μ, but they considered the band at 6·132 μ a fundamental of which the bands at 2·998, 1·967, 1·513 and 1·212 were harmonics, at the same time pointing out that the agreement was not particularly good. It might be mentioned that Barker, who had resolved the band at 2·998, found that it was of the same type as the band at 6·132 μ in that it had a well-marked Q branch, and that the wave-number spacing of the fine structure was the same as found for the band at 6·132 by Robertson and Fox.

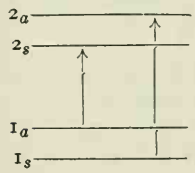
Mecke and Badger put forward the view that three fundamentals are the bands at 10·55 μ, 6·132 μ, and 2·998 μ, and consider the remaining bands as combinations of the frequencies represented by these wavelengths. If these combinations be compared with those of the observed bands, it will be found that the agreement, while perhaps better than that mentioned above, is still not very good, and the new bands obtained photographically by themselves and by Ellis fit in equally well as harmonics of the band at 6·132 μ as on their principle of combinations.

It is true that the application of the principle of combination gives an explanation for the occurrence of such a band as that at 2·264 to which no earlier simple harmonic or fundamental can be ascribed, but unless we are are going too fast, without waiting for information to be derived from the study of simpler molecules, the question is at present not clear, especially as the fine structure of some of these bands has not yet been worked out.

The speaker next invited discussion on the band at 15·908 μ, which Dr. Fox and he attributed to a rotation band, the influence of whose harmonics on the fine structure of the band at 10·55 μ they thought they had detected.

He then invited discussion on the structure of the band at 10·55 μ, which has two prominent Q branches, and as more recently shown by Barker, two sets of fine structure for the P and R branches. He would like further information on the suggestion of Barker that such an effort could be obtained by considering the nitrogen atom at one time above and at the other below the plane of the hydrogen atoms.

Professor Barker (*Michigan*), said : As suggested in the introductory paper of this section (see p. 899) the ammonia molecule probably has the form of a triangular pyramid of small altitude. Two of the four fundamental modes of vibration involve an oscillation of the N atom along the axis of symmetry, *i.e.*, normal to the plane of the three H atoms. The band at 10·5μ is associated with a symmetrical motion of the H atoms such that the distance between them increases when the N atom approaches the plane in which they lie. The equilibrium position of the N atom may be upon either side of this plane ; hence the potential energy function exhibits two minima separated by a relatively low maximum. Two *eigenfunktions* must therefore be associated with each vibration state, one being symmetrical and the other antisymmetrical. Because the two equilibrium positions are not far apart these two functions involve slightly different amounts of energy, and the vibration levels are all double. Finally, since transitions are always between states of opposite symmetry character, *e.g.*, $1_a \rightarrow 2_s$ or $1_s \rightarrow 2_a$, two absorption bands appear with slightly different frequencies.



The band at 3μ, which is probably associated with a vibration in which the three H atoms approach one another as the N atom approaches their plane, should also exhibit this effect, though in a much smaller degree, since the two potential energy minima are separated by a maximum rising considerably higher than before. Our resolution was insufficient to reveal this complexity. The doubling reported by Mecke and Badger in the band at 7900 Å. may be of this sort, however.

Professor O. S. Duffendack (*Michigan*), said : Although the recent work of Duffendack and Smith indicates that the electronic bands of carbon dioxide belong to the CO_2^+ ion, it may be well to keep them in mind when considering the form of the CO_2 molecule. The somewhat extensive system in which the bands occur in more or less irregular groups probably arises from transitions between the vibrational states of the several modes of vibration of which the molecule must be capable. The strong pair of bands near 2900 Å. has recently been photographed with large dispersion by J. F. Duncan at the University of Michigan. The details are soon to be published in *The Physical Review*. The

structure of these bands is very peculiar in that each band consists of a very sharp, intense centre line bordered on either side by nearly symmetrical fine structure, resembling R and P branches. These bands are quite different in structure from those of the extended system.

Mr. C. P. Snow (*Cambridge*), said: I should like to stress the practical necessity of the application of the Kramers-Heisenberg theory of dispersion to the Raman effect in gases. It is only by the "three level" scheme that the experiments of Wood and Rasetti upon HCl, CO_2, N_2O and NO can be explained; the actual infra-red bands have to be indirectly inferred from the observed lines.

Professor J. Errera (*Brussels*), said: I wish to draw attention to a device for the registration of infra-red absorption spectra which I have set up in my laboratory in collaboration with Dr. L. Marton. As source of illumination we have used a tungsten filament (taking about 0·5 kilowatts in an atmosphere of pure nitrogen) placed in metallic vessel with double walls through which water is circulated. This lamp is furnished with a fluorite window.

The pencil of monochromatic rays on leaving the spectrometer, is divided by two mirrors at an angle of 180°. One half traverses the cell containing the substance under investigation and is thereafter focussed by a NaCl lens and a mirror upon a Hettner microradiometer. The other half after travelling an analogous path, but without absorbent cell is focussed on a second Hettner microradiometer. The spots of light from the two instruments fall on a photographic registering cylinder. On the same cylinder there is projected an image provided by the spectrometer drum divided in μ, which indicates the corresponding spectral region.

One obtains, thus, on the photographic film three graphs corresponding respectively to the spectral region, to the incident rays, and to the same rays after absorption. In this way we are able to avoid the inconveniences which results from variations in the intensity of the illumination at source.

Professor R. Mecke (*Bonn*), said: With regard to Mr. Rawlins' paper (p. 925) I would refer to a paper of K. L. Wolf,[1] who uses exactly the same arguments in determining the form of the molecule and comes of course to the same result.

With regard to the paper of Professors Barker and Meyer (p. 912), I would like to remind the meeting that, as in the case of the ammonia band near 10μ, we have also found a doubling in the absorption band, $\lambda 7920$ Å., which is the third overtone of a fundamental band near 3μ. This doubling is, however, exceedingly small; *e.g.*, we can only find two different series having very slightly different spacing. We thought at first that this was due to a dissymmetry in the form of the molecule, but I now think it is due to the symmetrical and the antisymmetrical levels of the molecule. We have found a rather steep form of the pyramid, the angle between the height and the edge being 58°. I think this will account in our case for the small difference between the two levels.

As to Professor Ellis' paper (p. 888) I might say that there is surprisingly good agreement between the absorption bands in gas and in solutions of ammonia. We have studied the absorption of ammonia gas in the near infra-red[2] and found absorption bands at $\lambda 8810$, $\lambda 7920$,

[1] *Z. physik. Chem.*, 131, 90-96, 1927. [2] Page 936.

and λ6470, the first one is a very weak combination band, the two later correspond exactly to the two mentioned by Ellis at 0·795μ and 0·652μ. In analysing these bands we came to the conclusion that the band at 3μ ($\nu = 3336$) is the fundamental of these two bands and represents the vibration of the N—H bond. In addition to this Dickinson, Dillon, and Rasetti,[3] in studying the Raman effect of polyatomic gases, found in ammonia gas only one vibrational line corresponding to exactly the same value 3336 (in liquid ammonia they find two lines 3298·4 and 3214·5); I think these three entirely independent determinations confirm without doubt the existence of a fundamental frequency at $\nu = 3336$. For the same reasons I cannot agree with Sir Robert Robertson. Our bands below 1μ do not fit at all into the series with a fundamental at 6, 1μ. If this assignment is correct, the band at 8800 would be much stronger than that at 7920, but it is a very weak band. On the other hand, there is a band lacking at about 7100 which we could not find, although we were looking for it. Further I may call attention to the last table published in our paper, where I compare the frequencies of the X—H bonds in the stable molecules CH_4, NH_3 and H_2O with the corresponding frequencies of the unstable molecules CH, NH and OH, which were known to spectroscopists for some time. In passing from the unstable to the stable form a slight *increase* of the bonding forces takes place accompanied with a *decrease* of the nuclear distance.

SUMMARY.*

By Professor W. E. Garner and Professor J. E. Lennard-Jones.

The thirty-eight papers submitted for discussion cover the whole field of inquiry in molecular spectra and focus attention on some of the problems still outstanding. The discussion was particularly valuable as it brought together workers in the infra-red, visible, and ultra-violet regions and provided them with an opportunity of correlating their results with those recently obtained from a study of the Raman effect.

Notation of Molecular Spectra.

One of the most important questions to be discussed was that of notation, for the present lack of agreement causes much unnecessary difficulty in the reading of the prolific literature which is at present being published. R. S. Mulliken, F. Hund, and others have recently agreed upon a tentative scheme, which was presented by O. W. Richardson. The main object of this scheme is to devise a notation in as close harmony as possible with that already agreed upon for atomic spectra. The quantum numbers n and l are retained with meanings analogous to those used for atoms, and in addition a quantum number λ is introduced for the projection of l on the molecular axis. Small letters are used for individual electrons, and capital letters for the electron system as a whole. Thus, the resultant of the l values of individual electrons is denoted by L, and the resultant orbital angular moment round the molecular axis by Λ. The individual electron spins are denoted by s, and

[3] *Physical Rev.*, 34, 582, 1929.

* We wish to acknowledge our indebtedness to the editor of *Nature* for permission to make use of an article printed in the issue of 12th October, 1929.

the resultant by S, while the projection of S on the molecular axis is denoted by X. The quantum number of the sum total resultant angular momentum is denoted by J as in atoms. This consists of the electronic spin vector S and the resultant of orbital and rotation angular moments (together denoted by K). When individual electrons are known to have a definite angular momentum round the molecular axis, they are described as σ, π, δ, ϕ, . . . electrons according as $\lambda = 0, 1, 2, 3 \ldots$, in analogy with the s, p, d, f, . . . notation of atoms. For the molecule as a whole, the molecular states are denoted by Σ, Π, Δ, Φ, . . . according as $\Lambda = 0, 1, 2, 3, \ldots$, again in analogy with the S, P, D, F, . . . terms of atoms. Multiplicities are denoted as in atomic spectra, as, for example, $^2\Sigma$, $^4\Pi_{3/2}$.

There seemed to be general agreement among workers present at the discussion with regard to these main features, and criticism was directed mainly against other minor details. The modifications which Mulliken suggests should be made as a result of the discussion are the use of v in place of n for the vibrational quantum number, the use of a superscript number following the electronic term symbol as in $^2\Pi^3_{3/2}$ to indicate the vibrational quantum number and the addition in parentheses of the rotational quantum number (K or J), if need be.

It was urged in the discussion that a simplified notation was often desirable in experimental work, and to meet this need it was suggested that such symbols as $A^1\Sigma$ or $N^2\Pi$ might be sufficient, or even just A or N alone. A further suggestion is that transitions between molecular electronic states should be denoted in the form $^2\Pi \rightarrow {}^2\Sigma$ to indicate clearly the direction of transition. Those interested in polyatomic molecules urged that the notation adopted for diatomic molecules should be capable of extension to more general cases.

One welcome feature of the discussion was that it led to a general stock-taking of the present position, and stimulated workers to review the advances made in the last few years. O. W. Richardson gives a summary of the results obtained for the hydrogen molecule, of which about forty different electronic levels are now known, all of which are accounted for by current theories. W. E. Curtis presents an account of the present position with regard to the band spectrum of helium, the analysis of which is nearly complete in the visible and ultra-violet regions. This spectrum is particularly interesting, as it shows that the l vectors of the individual atoms gradually become uncoupled from the nuclear axis as the rotation of the molecule increases and tend to become coupled to the rotation axis. The transition from one case to the other gives rise to striking anomalies of structure and intensity. The theoretical significance of these anomalies is conveniently shown by the energy diagrams contributed by G. H. Dieke to the discussion (p. 776).

Apart from hydrogen and helium, the band spectrum which has received most attention is carbon monoxide, and at present sixteen band systems are known. A detailed account of these is given by R. C. Johnson, who directs attention to the recent discovery by Asundi of a quintet level $^5\Pi$ in this spectrum (the first quintet to be recorded in band spectra) and attributed the third positive carbon band system to a $^5\Sigma \rightarrow {}^5\Pi$ transition. This conclusion is important, because, if correct, it necessitates a modification of the electronic levels of the CO molecule hitherto accepted. Johnson proposes a detailed scheme for the electronic configurations of carbon monoxide in its various levels. He also indicates the states of the carbon and oxygen atoms after dissociation from each state.

Molecular Formation and Dissociation.

It is a matter of the greatest importance to the physicist and chemist to know what are the exact states of excitation of the component parts of a molecule on dissociation, for this knowledge can be used to control the reverse effect of combination. J. E. Lennard-Jones proposes an *Aufbau* principle for a number of diatomic molecules which provides this information. This investigation shows on theoretical grounds that some molecules would be expected to dissociate into normal components, others into one or more excited components. The molecular ion N_2^+, for example, would be expected to dissociate from its normal state into one *normal* N atom and one *excited* N ion, and it has been shown recently by Heitler and Herzberg that the experimental results point to the same conclusion. Other cases where a normal molecule separates into excited atoms were given in a paper by E. Bengtsson and E. Hulthén (Stockholm), who describes some new results obtained for the spectra of some metal hydrides (CuH, AgH, AuH, etc.). A typical result is that CuH separates from its normal $^1\Sigma$ state into an excited Cu atom ($^2D'$ state) and an H atom in a $3d$ level.

F. Hund (Leipzig) contributes a paper on the general criteria for chemical binding. Theoretically, it is now possible by the new quantum mechanics to work out the interaction of two atoms in a molecule, but actually the calculations are so involved and so laborious that they have been carried out only in one or two simple cases, and it is desirable to have other simpler methods to indicate whether two atoms can combine to form a stable molecule or not. A method successfully used by Hund in many cases can be illustrated by considering the two pairs of atoms H + H and He + H in their fundamental states. One can form a molecule (H_2), the other probably not (HeH). The characteristic difference may be ascribed to the change in binding of the electrons in the two hypothetical processes: $H + H \rightarrow H_2 \rightarrow He$, and $He + H \rightarrow HeH \rightarrow Li$. In the first case, the binding of the electrons increases in the transition from the separated atoms to the united atom, while in the second case the binding of one of the three electrons is considerably diminished.

One of the interesting results of the work on band spectra is the determination of heats of dissociation. It has been observed that sets of vibrational levels often approach a point of confluence, that is, the separation of successive levels approaches zero, and it is now generally agreed that at the point of confluence one portion of the molecule (usually an atom) is separated from the remaining portion. If the vibrational energy levels can be followed up to, or almost up to, the point of confluence, the energy required for dissociation from the electronic level concerned becomes known. The ordinary heat of dissociation, as defined by the chemist, can then be deduced when the energy content (that is, the state of excitation) of the dissociated atoms is known. Unfortunately, it is not always possible to obtain a full set of vibration energy levels up to the limit of dissociation, and when only an incomplete set can be obtained, special methods have to be employed to infer the correct interpolation to dissociation. The most successful of these methods was given by Birge and Sponer three years ago and applied to nitrogen, oxygen, carbon monoxide, and other molecules. An improved method is now suggested by R. T. Birge which is described in a communication to the discussion. The essential point of the paper refers to a new method of plotting the frequency of vibration, which, it is claimed, leads to more trustworthy values of the heat of dissociation. The most probable

values of the heats of dissociation of nitrogen and oxygen are now given as 9·1 volts and 6 volts respectively. Out of this investigation has emerged the fact that in many cases the plot of the frequency differences against quantum number possesses a point of inflection, which it is suggested, is due to a discontinuity in the process of dissociation; it is considered that at the discontinuity, a molecular rearrangement occurs. R. C. Johnson, in the discussion suggests that the critical point marks the change from quasi-molecular to true atomic conditions within the component atoms.

The band spectra of polyatomic molecules show a more gradual transition from band to continuous spectra. V. Henri and his colleagues find that with complex molecules the bands become *diffuse* before passing into a continuous spectrum. These diffuse bands are attributed to a loss of rotational quantisation. V. Henri employs the term "predissociation" to indicate the state of the molecule after receiving energy corresponding to the wave-lengths in these diffuse bands, and brings forward evidence to show that in this state the molecule is photochemically active. He concludes that the vibrational bands become diffuse on account of a molecular rearrangement which takes place within a time interval which is less than the period of rotation but greater than the period of vibration of the molecule. This rearrangement may consist of dissociation into atoms or may be due to some change of molecular level. In a discussion of the above phenomena, V. Henri shows that the production of diffuse spectra is favoured by raising the temperature. A paper by S. Barratt reports the occurrence of similar diffuse bands in the spectra of the molecules formed by zinc, cadmium, and mercury with the alkali metals, and also Herzberg finds similar bands in the ultra-violet absorption spectra of the methyl halides. Herzberg suggests that the state of predissociation occurs only when the energy content of a molecule is higher than the dissociation energy of the normal state.

Ellis applies the methods of Birge and Sponer to the calculation of the heats of dissociation of C – H and N – H groups in organic compounds. The results are in agreement with thermal data and indicate that the heats of dissociation of these groups are dependent on chemical constitution.

A paper by Goodeve and Stein on the absorption spectrum of chlorine dioxide provides an interesting example of a change of slope on the frequency difference-quantum number curve. This is of a different type from that discussed by Birge. The rotational structure of the vibrational bands disappears at the point of change of slope; thus these experiments link up with those of V. Henri on predissociation.

Band Spectra and Atomic Nuclei.

The study of band spectra promises to be a valuable source of information about the masses and structure of nuclei, and in particular seems likely to lead to the discovery of many new isotopes. The rapid advances which have been made in this field during the past year are summarised by R. T. Birge. Already it has been established that there are oxygen isotopes of mass 17 and 18, and that carbon has an isotope of mass 13. It may be that *all* elements have isotopes, although the agreement of Aston's mass determinations with the usual chemical atomic weights proves that any isotopes as yet unknown can only be present in very small amounts. For the detection of such faint isotopes, the analysis of band spectra seems superior to the mass spectograph, though, as band spectra give only *relative*

masses of two isotopes, the two methods must be used to supplement each other.

The evidence of band spectra as to the *spins* of nuclei is summarised in a paper by R. S. Mulliken. In the spectra of molecules which contain two nuclei, equal both in charge and mass, every other line in each series of band lines is relatively weak or else missing. Heisenberg and Hund have suggested that this phenomenon can be explained by assuming that a necessary condition of existence for any state of a molecule is that it be antisymmetrical in all protons as well as in all electrons. The correctness of this antisymmetry rule for the extra-nuclear electrons in atoms is well established by the facts of line spectra. Its applicability to protons is confirmed by the specific heat and band spectrum data for hydrogen, but whether it applies to protons and electrons in complicated nuclei is still doubtful. There are difficulties in the case of N_2. In most cases the alternating intensities observed in the Raman effect are in complete agreement with those of band spectra and in accord with theoretical expectations; but for nitrogen, Rasetti finds that transitions between the even levels of the ground state are more intense than those between the odd levels. As nitrogen in the ground state is $^1\Sigma$ like H_2, and from the constitution of the nuclei would be expected to have a nuclear spin like that of hydrogen, the result seems to be in conflict with the rule given above.

It seems as if the *eigenfunktion* of the nitrogen molecule is symmetrical in the nuclei. This means that the nitrogen nuclei follow the Bose statistics, whereas, as pointed out by Mulliken, they would be expected to follow the Fermi statistics, because they contain an odd number of particles which follow the Fermi statistics. G. Herzberg gives the recently published views of Heitler and himself that in the nucleus the electron not only loses its spin (as shown by Kronig) but also its influence on the statistics. If true, this is a new and remarkable result.

The isotope effect in chlorine compounds is discussed by Patkowski and Curtis for the absorption spectrum of ICl, by V. Henri for $COCl_2$, and by Goodeve and Stein for ClO_2. Patowski and Curtis show that, for molecules where relatively large quantum numbers occur, the isotope separation of band heads reaches a maximum for a particular value of the vibrational quantum number. From the location of the maximum the true n' values may be calculated. Use is made of this fact to obtain the true vibrational quantum number for bands in the ICl spectrum.

The Raman Effect.

The discussion on the Raman effect was opened by Sir C. V. Raman and papers were contributed by R. W. Wood, J. Cabannes, P. Daure, H. S. Allen, A. M. Taylor, and A. C. Menzies. Raman gives a historical survey of his discovery and emphasises the necessity for linking up the effect with the diamagnetic susceptibility and optical anisotropy of crystalline substances. The new method has opened out many possibilities of development for the chemist, in particular in the direction of increasing our knowledge of the vibration frequencies and structure of organic molecules. The light scattered when a beam of monochromatic radiation passes through gaseous, liquid, or solid media is resolved into a series of bands of frequency, $N \pm n$, and n is attributed to the characteristic rotation and vibration frequencies of the medium. The agreement between the values of n and the frequencies of the infra-red bands is evidence of the correctness of this interpretation. It is, however, one of the important features of the Raman

effect, that the frequencies of the scattered radiation indicate the existence of vibrations in molecules which are optically inactive in absorption. These had already been inferred, but could not be demonstrated from the infra-red spectra. For example, Schaefer shows in his paper that the infra-red vibration levels of the CO_3 ion can only be interpreted on the assumption that a number of the absorption bands are due to inactive vibrations occurring in combination with active vibrations. The frequency of the optically inactive fundamentals which is required for adequate explanation of infra-red spectra, is precisely that which is found in great strength in the Raman effect. A parallel case is that of the molecule of carbon dioxide, the optically inactive vibration of this molecule coming out strongly in the Raman spectrum (Rasetti).

The value of the Raman spectrum for the analysis of the ultra-violet spectra of organic compounds is referred to by V. Henri. It is important in such analysis to know what are the fundamental frequencies of the inactivated molecules and these are given by the Raman spectra.

McLennan finds, in the Raman spectrum of ordinary liquid hydrogen, the two rotational transitions, $0 \rightharpoonup 2$, and $1 \rightharpoonup 3$, the latter being the stronger. The relative intensities of the two lines are explained if there are two to three times as many molecules in the first quantum rotational state as in the zero rotational state. The result is in agreement with that deduced from the specific heat of hydrogen gas with regard to the relative weights of the odd and even rotational levels.

The high degree of dispersion which is possible by the Raman method, has resulted in the separation of the C – H bands into several components. Raman showed spectra in which this band is resolved into four clearly distinguishable components, a resolution which has also been effected by Petrakaln and R. W. Wood. The latter contributes a paper in which the improvements in experimental technique necessary to obtain this result were described.

It was emphasised that the frequencies of the lines due to C – H in aromatic and aliphatic compounds are different, and the degree of polarisation strikingly so. The lines from cyclohexane are intermediate between those of aromatic and aliphatic compounds. The theory of the intensities and degree of polarisation of the Raman lines receives attention in papers by Cabannes, who emphasises the value of the spectra in amplifying the information about crystal structure which is gained by the X-ray method. Daure directs attention to the differences between the spectra of liquids and gases, and points out the importance of the effect in the study of the association of liquids. R. Mecke has supplemented the results of Daure on the differences between the spectra of gases and liquids by a table of results for ammonia, water, methane, ethylene, and the SO_4 ion. A. M. Taylor's work on the Raman lines of AX_4 ions shows that the frequency of vibration is diminished on destruction of the crystal lattice and on hydration of the group, and Menzies describes experiments in which measurements had been made of the Raman effect with powdered crystals (see also *Nature*, Oct. 5, p. 511).

Structure of Unexcited Molecules.

In the last few years there has been a rapid advance in our knowledge of the rotational and vibrational levels of molecules in the unexcited state. The study of infra-red absorption spectra has revealed not only the magnitude of internuclear distances and the nature of structural arrangements in space, but also has yielded precise information about the rotational and

precessional movements of molecules. Detailed knowledge is at present limited to simple molecules in the gaseous state. For complex organic molecules, studied in the solid or liquid state, only the vibrational levels have been systematically examined, such as those of C – H, C = O, C – OH, N – H, C ≡ N groups, and the manner in which the frequency of these levels changes with modification in chemical constitution. In an introductory address on the infra-red spectra of gases, Sir Robert Robertson outlines the advances so far made, especially with reference to their bearing on chemical problems. E. K. Rideal also surveys the recent advances in this field, which are of interest to chemists.

E. F. Barker and C. F. Meyer, in a survey of the experimental investigations on the vibration bands of simple molecules in the gaseous state, propose a method of classification of molecules into groups according to the complexity of the rotational levels. Diatomic and linear molecules like carbon dioxide and acetylene only rotate in a plane and show no precession. Methane, on account of its symmetry, can rotate about any axis without precession, but, in general, polyatomic molecules rotate with a precession, the complexity of which depends on the molecular symmetry. Ammonia, ethane, methyl fluoride, etc., which have symmetry about one axis of rotation, give a less complex rotational structure than water, sulphuretted hydrogen, and ethylene, which possess three unequal moments of inertia. It is a curious fact that carbon dioxide is linear, while water is a triangular molecule.

A noteworthy advance in the interpretation of molecular spectra has been made by the application of the conception of nuclear spin. The acetylene bands exhibit a striking example of alternating intensities which are analogous to those observed in molecular hydrogen and can be explained in a similar way. The two hydrogen protons of acetylene, both spinning in directions parallel to the axis of rotation, may have either the same, or opposite, spins. Thus there seem to be two types of acetylene molecule, just as there are two types of the hydrogen molecule. The bands of molecules like methyl fluoride and ammonia, which have triple proton symmetry about a rotation axis, show every third rotation level intensified.

The double Q branch of ammonia at 10·3 μ and 10·7 μ was discussed by Robertson and Barker. The view expressed by Barker is that the ammonia molecule probably has the form of a triangular pyramid of small altitude. Two of the four fundamental modes of vibration involve an oscillation of the N atom along the axis of symmetry, *i.e.* normal to the plane of the three H atoms. The band at 10·5 μ is associated with a symmetrical motion of the H atoms such that the distance between them increases when the N atom approaches the plane in which they lie. The equilibrium position of the N atom may be upon either side of this plane; hence the potential energy function exhibits two minima separated by a relatively low maximum. Two *eigenfunctions* must therefore be associated with each vibration state, one being symmetrical and the other antisymmetrical. Since transitions are in this case between states of opposite symmetry character, *e.g.*, $1_a \rightarrow 2_s$ or $1_s \rightarrow 2_a$, two absorption bands appear with slightly different frequencies.

F. I. G. Rawlins, surveys the facts now known with regard to the infra-red absorption spectra, molecular heats, and electric moment of carbon dioxide and concludes that this molecule is linear. In a paper on the vibration-rotation spectra of diatomic molecules C. P. Snow draws attention to the occurrence of a Q branch in the rotation vibration

spectrum of nitric oxide which is attributed to the fact that this molecule contains an odd electron.

Mecke and Badger have succeeded in photographing the higher harmonics of the frequency bands of ammonia in the near infra-red. The fine structure of these bands is analogous to that of bands in the further infra-red. This is a marked advance in the technique of the study of vibration bands.

The Liquid State.

The advances made in our knowledge of the structure of the molecules of liquids by means of Raman spectra has already been referred to. The Raman spectra of liquids agree in their main features with the infra-red spectra and from both information with regard to the vibration levels can be obtained. Jean Lecomte in an introductory paper on the infra-red spectra of liquids summarises the experimental results so far obtained in this field.

The vibration levels of the C – H, N – H, C = O, etc., groups are now known, due to the labours of Bonino, Lecomte, Ellis, Sallant, and others, and by the Raman method it is found that the C – H levels are multiple. There appears to be a level for each C – H group in the molecule, the greatest difference in frequency occurring between the levels of C – H in aliphatic and aromatic compounds. G. B. Bonino discusses the effect of chemical constitution on the fundamental frequency of this group, and considers the effect of lengthening the carbon chain, of the presence of the double linking between carbon atoms, and the influence of hydroxyl and halogen substitution. The extinction coefficients of the absorption bands are found by Bonino not to be proportional to the number of groups in the molecule; investigation of the individual C – H levels from this point of view has yet to be undertaken.

The Solid State.

In an address on the infra-red spectra of solid bodies, C. Schaefer summarises the information so far obtained with regard to the frequency of vibration of crystal lattices and the vibration of atoms composing physically distinct groups in the crystal. The detailed investigations of Schaefer on the crystalline carbonates and nitrates have brought to light the optically inactive vibrations of the CO_3 and NO_3 ions, and also have indicated in what manner the vibrations of the atoms in these groups depend on the crystal symmetry. The main features of the vibrations of these groups, their frequency, for example, are but little affected by the cation. This is in accord with the structure of these ions as deduced by X-ray analysis. In uniaxial crystals, however, the frequency bands are doubled, and this may mean that the equilateral of the CO_3 ion is distorted, though this has not hitherto been detected by Röntgen analysis. The infra-red spectroscope may, therefore, be used to supplement researches with X-rays.

Water of crystallisation gives nearly the same frequencies of vibration as liquid water, but the bands are doubled in uniaxial and tripled in biaxial crystals, showing that the symmetry of the water molecule partakes of that of the crystal as a whole.

A. M. Taylor describes experiments made on crystals containing the group AX_4. SO_4, CrO_4, ClO_4, and MnO_4 groups give very similar absorption spectra. There are two fundamental vibrations for these groups which are optically active, and one which is optically inactive.

REVIEWS OF BOOKS.

Photo-processes in Gaseous and Liquid Systems. By R. O. GRIFFITH, D.Sc., and A. McKEOWN, D.Sc. (Longmans, Green & Co. Pp. viii and 691. Price 25s. net.)

In many modern photochemical investigations the Starck-Einstein law of equivalence in photo-excitation is taken as a fundamental concept and interest is focussed on the reasons for any discrepancies between the amount of chemical action obtained and that anticipated. A brief consideration, however, indicates that it is probably more important to obtain information as to what is the exact mechanism of photo-excitation and to understand what effects changes in the energy content in the electronic, vibrational or rotational states of the molecule may have both on one another as well as on the molecular stability and reactivity.

Thus a well-balanced book on modern photochemistry should contain an account not only of what is generally considered as photochemistry but also of atomic and molecular spectra and should include a detailed treatment of such subjects as the formation of excited and metastable atoms and molecules, fluorescence and resonance radiation. In respect both to general arrangement and the general treatment of the subject I consider that this volume is by far the most satisfactory one that has as yet been published in any language and is a credit both to the authors, the editor and the publishers. Almost half the book is devoted to a description and analysis of the results of the spectroscopic investigations.

Molecular spectroscopy has been divorced from photochemistry for such a long period of time that it is admittedly difficult for anyone to keep *au fait* with the more modern developments in both fields, and the reader cannot help being inclined to be somewhat critical of one or other portion of the book. Whilst the treatment of the quantum theory and of atomic spectra (Chs. II. and III.) is clear and satisfactory, that on the spectra of molecules (Ch. IV.) cannot be considered as up to the same standard. Many important advances both in the treatment of the electronic and especially of the vibrational rotational spectra of molecules have been made in the last two and a half years, some of which might well have been included in a volume published in August of this year. Whilst interest in treatment of band spectra is not universal these omissions, whilst leaving many points, which have now been settled, in a state of obscurity in the volume, are not so serious as some others which are more utilitarian in character. Some mention might have been made of Turner's valuable method of evaluating the life of an excited species from the influence of pressure on the quantum efficiency, and the data on the convergence limits of molecules which gives us valuable information on the molecular heats of dissociation are those employed in 1926. Thus whilst some doubt exists as to the heat of dissociation of the normal nitrogen molecule the value of 11·4 volts is certainly too high. The value obtained by Birge from Herzberg's work and by Gaiola on the negative band spectrum, *viz.* 9·5 volts, is in agreement with Kaplan and Cario's work on active nitrogen although more recently a value of 8·5 volts has been proposed. A similar comment may be made concerning oxygen, for which Herzberg's value of 6·5 volts appears preferable to the 7·02 volts of Birge and Sponer.

Such data are important in view of the increasing tendency to discuss the possibilities of certain chain reactions in the light of the thermal magnitudes involved in each chain link. The important radical "hydroxyl" might well have been included and more space devoted to the phenomenon of predissociation. Chapters V. and VI. on fluorescence and chemiluminescence contain valuable information clearly presented. In the latter chapter one notes the mention of the Wedekind reaction, the interaction of chlorpicrin and a Grignard reagent, as an important example of chemiluminescence on account of the brightness of the light emitted. The reaction is an unpleasant one to carry out and the flash although vivid is of short duration ; the oxidation of many dyestuffs by ozone is be preferred as an example of an effective chemiluminescent reaction. The light emitted in this case is vivid and bright and of long duration, the mechanisms in either case judging by the complexity of the band system must be complex.

The second six chapters in the book, are devoted to systematic photochemistry including three excellent chapters, two on Einstein's Law (VIII. and IX.) and one on photo-sensitisation (Ch. XI.).

The summary of the various views and of conflicting experimental evidence in reactions such as the hydrogen chlorine reactions have been ably and fairly presented and the authors own comments on several points raised in these controversal reactions are keen and critical, an indication of real thought.

The volume is uniform with the Ramsay series now edited by Professor Donnan and is certainly worthy of being included in that excellent collection.

Infra-Red Analysis of Molecular Structure. By E. I. G. Rawlins and A. M. Taylor, with an introduction by E. K. Rideal. Pp. xv + 176. Cambridge : (The University Press). 10s. 6d. net.

Although a large body of investigations in infra-red spectroscopy and allied problems has been published since the pioneer work of Coblentz a quarter of a century ago, it is only within the last few years that the significance of the relation of infra-red spectroscopy to molecular structure has received full recognition. It is the purpose of the present volume to place before the reader a summary of the work done so far, its interpretation and the methods whereby the experimental data may be used to interpret molecular structure. An excellent introductory chapter by Dr. Rideal opens the book. It is noted that the preface and introduction are inclined to be apologetic ; this is entirely unnecessary, seeing that the volume brings together information not readily accessible to the reader, in a field which is only now beginning to receive the attention it deserves. The book gives a general account of infra-red absorption spectra of gases, liquids and solids, together with the experimental arrangements necessary for accurate work. In writing these accounts the authors have had the advantage of an intimate acquaintance with the experimental difficulties. Their descriptions and comments are therefore written with knowledge. It is, however, the theoretical aspect of the subject that receives the authors' attention to a large extent, thereby giving a readable essay on molecular structure. The discussions are set out clearly, the reader being introduced to the conventional notation adopted for expressing rotation spectra and rotation vibration spectra (p. 10). The classical work of Randall and Imes and of Czerny on the halogen hydrides is recounted fully with an adequate explanation of the fine structure of the bands and its relation to the structure of the molecules both in rotation and in vibration. Half-quanta are introduced very early with Czerny's demonstration of the necessity of half-quanta for the pure rotation spectrum of diatomic molecules. Work on gases is perhaps

the most satisfying in the infra-red as being capable of yielding results from many different directions leading to similar molecular models. The chapter on the infra-red spectra of liquids is mainly descriptive, as is to be expected from the difficulty in interpretation of the vast body of results available. Solids receive adequate treatment, discussion being specially devoted to the characteristic frequency of crystals (p. 80 *et seq.*). In this important branch of the subject the work of Schaefer and others on the carbonates receives attention, as does the demonstration of Taylor and Rideal that many bands between 8μ and 14μ are merely the results of interference due to the thickness of the crystal under examination. It is also shown how the infra-red spectrum of crystals may be used to investigate the dynamic behaviour of component parts of crystals. Some thirty pages are devoted to the experimental procedure in making infra-red observations, the description being sound and full of useful hints. It describes the difficulties inherent in the apparatus required, the methods of obviating mechanical vibration, the relative merits of the receivers of the radiation and the various types of spectrometer in use. The book ends with a mathematical appendix consisting of some notes useful to those who desire to pursue the subject. A short account of Schrödinger's wave-mechanics is given. This section might well have been extended to include a worked example or two showing how it is actually employed in practice.

This book comes at an opportune moment. The Raman effect cannot be understood fully by the reader unless he has some acquaintance with the work in the infra-red region of the spectrum. It is impossible for example to appreciate the significance of the discovery by Wood of the missing Q line in the Raman spectrum of HCl, unless one understands the significance of Imes' observations on the rotation vibration spectrum of HCl, with its missing line. In the same way the recent discovery of Raman lines corresponding to "inactive" frequencies in crystals is of the utmost importance in the study of structure. From the foregoing it will be seen that this contribution to the literature of infra-red spectra is to be commended and should be in the hands of those who desire to follow recent developments in the study of the structure of molecules. The volume is not too difficult to be followed by the average reader or student of physical chemistry, it has adequate references and serves to introduce the subject to those who may desire to continue it at a later stage.

J. J. F.

La Diffusion moléculaire de la Lumière. By JEAN CABANNES (with the collaboration of YVES ROCARD). Pp. viii + 326. (Paris : Les Presses Universitaires de France. Price 65 fr.)

Although the idea of the molecular diffusion of light is quite modern there exist to-day a very large number of investigations on the subject. The first discussions arose in connection with the blue of the sky, the experiments of Tyndall, and the theory of scattering developed by Lord Rayleigh. Although at first this scattering was attributed to particles of dust, germs, etc., accidentally present in the atmosphere, it ultimately was realised that, although such accidental particles play their part, the blue of the sky is intense even when they are absent. In such a case the molecules themselves (which introduce heterogeneity in the case of a gaseous medium) become the scattering elements, and the measurements of Abbot and Fowle, in the clear air of Mt. Wilson in fine weather, have demonstrated (1910-11) that the number of scattering particles is

equal per unit volume to the number of molecules of air. The calculation was based upon the late Lord Rayleigh's theory of scattering of light. This result was quite contrary to the conception of Tyndall who considered that air devoid of dust, etc., would behave as an absolute vacuum to light.

When once this is admitted for a gas it must be expected that liquids will also produce a molecular scattering. Rayleigh, however, showed that the simple theory that he had developed would not hold good for liquids because the scattering centres could no longer be considered as being independent of each other.

The present volume describes experimental and theoretical investigations begun by the author in 1913 together with a full historical and critical account of anterior work and of the later work of others on the same question. The importance of the scattering can be realised from the statement that the scattering in water (liquid) is roughly 200 times that of the same volume of air; and that of benzene is 2000 times. A cubic metre of liquid benzene in bright sunshine would therefore behave as a *source* of 100 candle power. The difficulties of observation are not very great; what is difficult is the perfect purification of the liquids and it is of course essential completely to exclude extraneous light.

It is impossible in a short notice to give more than an indication of the contents of the book. The author is very careful to attribute to others the credit that is due them. In connection with liquids this includes the work of Smoluchowski, Einstein, W. H. Martin, Rocard, Raman, Ramanathan, R. Gaus, and many others. Rocard contributes two chapters on the "molecular field" and on opalescence near the critical point.

Cabannes is well aware that though he and other workers have done much to clear up the problem there is much still to be done. He considers his book as modestly indicating one stage—it is a point of departure for new efforts. With the hope of encouraging further research he points out the defects in present experiments and theory. It is none the less true that the results already obtained are very great.

The volume includes a very complete bibliographical index.

At Home among the Atoms. A First Book of Congenial Chemistry. By JAMES KENDALL, M.A., D.Sc., F.R.S. (London: G. Bell & Sons, Ltd. Pp. xv and 270. Price 7s. 6d. net.)

Most chemists and physicists have at some time found themselves trying to explain the modern conception of the atom to those devoid of any knowledge of science. The tale is vastly interesting to the teller and can be made interesting to the auditor: but much depends upon the manner of the telling and not all of us are able to avoid the glassy eye of uncomprehending but polite attention—or worse.

Professor Kendall has a sense of humour and has assuredly found the right manner of telling. He leads the reader from that state of knowledge when it is necessary to explain the difference between physical admixture and chemical combination up to a reasonable conception of the Bohr atom—or "Bohrville," as he terms the garden city to which the elements have been moved from the crowded "apartment house" of the periodic classification. Then he leads beyond to what he terms "the first hills leading upward to the highest mountain peaks of present-day chemical discoveries." It is, perhaps, a pity that this book was not written before the Schrödinger conception, because the reader may

possibly feel that the summit on which he is left is still somewhat in the clouds ; but that is not Professor Kendall's fault—no guide could have shown the way more clearly.

The journey is beguiled with humorous quip and fantastic but apt analogy to such an extent that the traveller does not realize he is treading the path of knowledge. Some might dub their guide flippant ; to those who like their science stern and serious, he may be ; but he is interesting and he is clear.

Perhaps the best appreciation the reviewer can give is to relate that he has the utmost difficulty in retrieving the book from borrowers. It is not a book which is put aside and forgotten ; every member of the borrower's family wants to read it, once a few of the inevitable extracts have been read aloud.

The scientific purchaser will probably look at the Chapter Titles and Head-notes and will chuckle ; then he will assuredly read the book through from cover to cover before passing it on to the friend for whom it was intended—and will probably buy another copy for his own library.

Proceedings of the Seventh International Congress of Photography. (London, July 9-14, 1928.) Edited by W. CLARK, T. SLATER PRICE and B. V. STARR. (Published for the Congress by W. Heffer & Sons, Ltd. Pp. xiii and 571. Price 25s. net.)

The report of the Proceedings is printed in the appropriate sections as follows :—

Section 1a.—Theoretical Aspects of Photography (including the theories of sensitivity and the latent image, photochemical questions, density measurement etc.)—26 papers read and discussed in 6 sessions.

Sections 1b and 1c.—Photographic Practice and Scientific Applications of Photography—18 papers and 3 sessions.

Section 1d.—Photo-engraving—10 papers and 2 sessions.

Section 3.—Bibliography, History, etc.—8 papers.

It is impossible to review the many valuable papers and reports which were contributed ; it may be said, however, that contributions were made by most of those who took part in the Faraday Society's General Discussion in 1923 on the Physical Chemistry of the Photographic Process so that to an extent the volumes may be treated as complementary.

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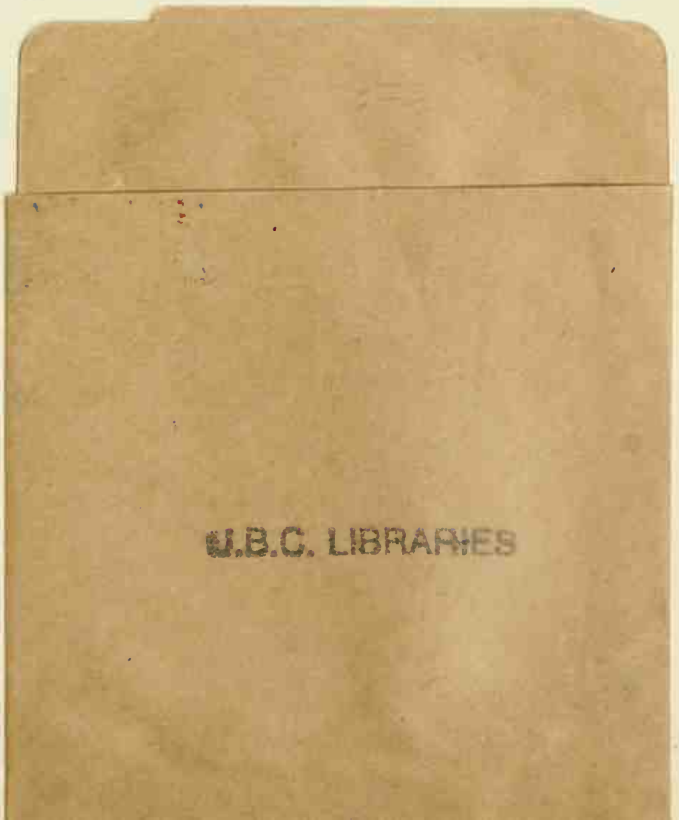
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